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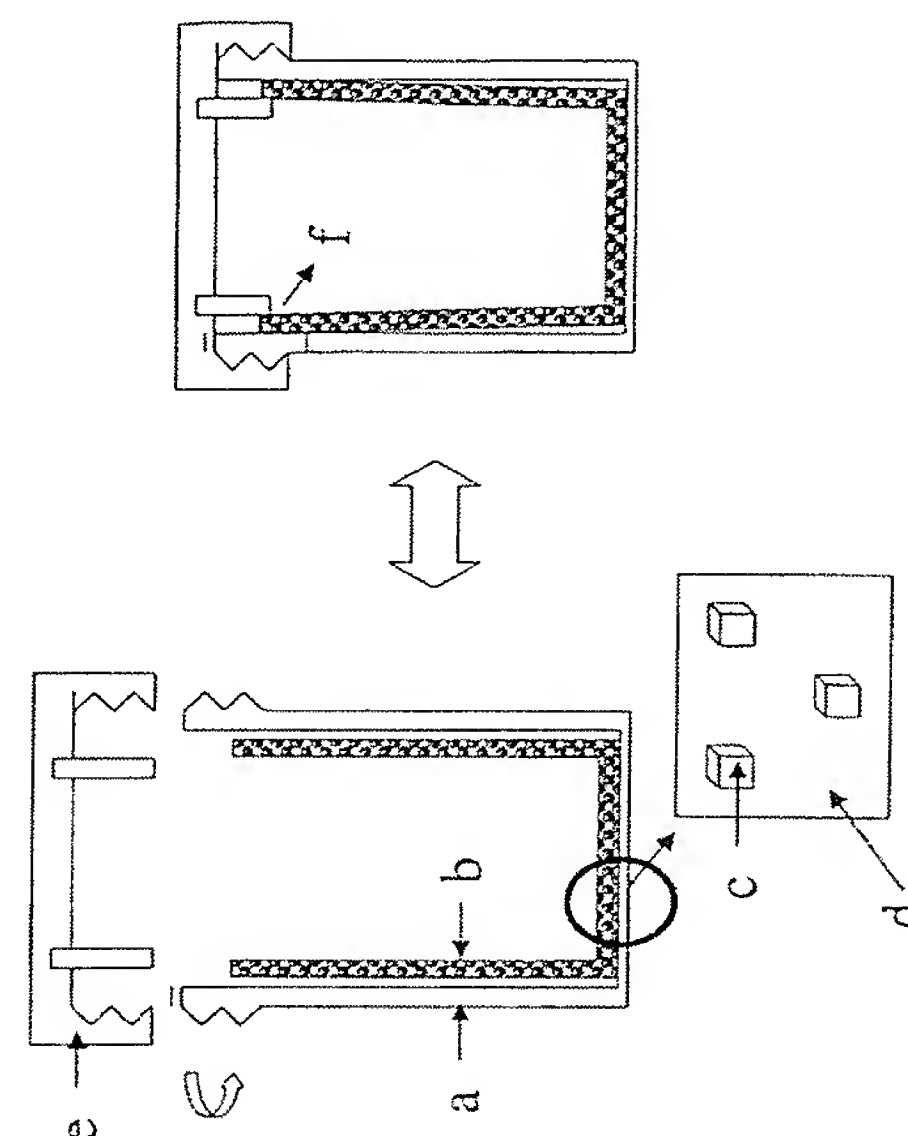
(54) 【発明の名称】 吸湿機能かつインジケータ機能を有する樹脂組成物およびそれを用いた積層体、包装体

(57) 【要約】

【課題】 組成物としての強度物性の改善させながらも、インジケータ機能および吸湿機能を有する事が可能な樹脂組成物およびそれを用いた積層体、包装体を提供することが望まれていた。

【解決手段】 シクロペンタジエニル誘導体の特定遷移金属原子からなる錯体もしくは、上記金属錯体に必要に応じてメチルアルミノキサンからなる、シングルサイト触媒を用いて得られたエチレン- α オレフィン共重合体を必須成分として含む等のポリオレフィン樹脂を主成分とし、これらの樹脂100重量部に対し少なくとも吸湿機能を有するゼオライト等の無機化合物を1～100重量部含有する樹脂組成物において、吸湿前後における色の变化(色差=ΔE)が少なくとも3以上である吸湿機能かつインジケータ機能を有する樹脂組成物を提供する。

【選択図】 図1



【特許請求の範囲】

【請求項 1】

ポリオレフィン樹脂を主成分とし、これらの樹脂 100 重量部に対し少なくとも吸湿機能を有する無機化合物を 1 ～ 100 重量部含有する樹脂組成物において、吸湿前後における色の変化（色差＝ ΔE ）が少なくとも 3 以上である事を特徴とする、吸湿機能かつインジケータ機能を有する樹脂組成物。

【請求項 2】

吸湿機能を有する無機化合物が合成あるいは天然ゼオライトである事を特徴とする、請求項 1 記載の吸湿機能かつインジケータ機能を有する樹脂組成物。

【請求項 3】

主成分となるポリオレフィン樹脂が、シクロペンタジエニル誘導体の周期律表第 I I I、I V、V、V I、I X、X 族遷移金属原子からなる錯体もしくは、上記金属錯体に必要に応じてメチルアルミノキサンからなる、シングルサイト触媒を用いて得られたエチレン- α オレフィン共重合体を必須成分として含むことを特徴とする、請求項 1 または 2 記載の吸湿機能かつインジケータ機能を有する樹脂組成物。

【請求項 4】

請求項 1、2、または 3 記載の樹脂組成物層を設けたことを特徴とする積層体。

【請求項 5】

請求項 1、2、または 3 記載の樹脂組成物層のどちらか一方に、ポリエチレン、エチレン- α オレフィン共重合体、ポリプロピレン、プロピレン- α オレフィン共重合体、エチレン-環状オレフィン共重合体、アルミ箔、アルミ蒸着フィルム、無機化合物蒸着フィルムなどの防湿層を設けたことを特徴とする請求項 4 記載の積層体。

【請求項 6】

請求項 4 または 5 記載の積層体から形成された包装体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は吸湿機能かつインジケータ機能を有する樹脂組成物およびそれを用いた積層体、包装体に関し、さらに詳細には、吸湿に伴う発色が鮮明でかつ、吸湿速度が良好なことから吸湿能力に優れる、樹脂組成物、あるいはこれら樹脂組成物を用いた積層体、包装体に関する。

【0002】

【従来の技術】

各種内容物を包装するパッケージ事業という分野において、「パッケージ」あるいは「包装」の要求内容としては大きく以下の内容が挙げられる。

【0003】

(1) 消費者に対する購買意識の付与、危険性の提示といった「表示効果」

(2) 充填した内容物自体に包装体が侵されないための「内容物耐性」

(3) 外部刺激に対する「内容物の保護」

これらの要求内容は更に細分化され、細かい要求品質へと展開される。そのうち、「内容物の保護」という点で特に注目を浴びているのが、酸素や水分からの内容物の保護が挙げられる。特に最近では、食品分野、工業製品分野、医療・医薬品分野等の各分野において、酸素や水分に対する内容物の保護性が重要視されるようになってきた。その背景として、酸素については酸化による内容物の分解、変質、水分については吸湿や加水分解に伴う内容物の変質が挙げられる。

【0004】

このように酸素あるいは水分による内容物の変質を防ぐ為、様々な方法が検討されてきた。その一つが、酸素バリアあるいは水分バリア性を有する材料を用いた包装体を設計することが挙げられる。水分バリアという点で例を挙げると、防湿性のあるポリオレフィン系樹脂を用いる、あるいは、これらのポリオレフィンやポリエステルやポリアミドフィルム

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にポリビニリデンクロライド系コーティング層を設けることで防湿性を付与したフィルムが最も一般的である。

【0005】

これらの水分バリア性基材を用いた包装体は、その高い水分バリア性から各種用途に展開が広がっている。しかしながら、これらの水分バリア性基材は塩素系ポリマーを用いていることからその代替案が検討されている状態である。

【0006】

また、一部の内容物によっては、ヘッドスペース中のわずかな湿度や水分によって劣化を伴う場合もあり、包装容器外側からの水分バリア性だけでなく、ヘッドスペース中の湿度や水分も除去したいというニーズが出てきている。

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【0007】

このような背景から、極度に吸湿を嫌う内容物、例えば吸湿食品や医療または医薬品やエレクトロニクスデバイスなどの工業製品分野においては、シリカゲルや酸化カルシウムなどの吸湿剤を不織布や透湿性の優れる包材に包装した小袋状の吸湿剤を、これら吸湿を嫌う内容物とともに包装しているのが現状である。

【0008】

特に塩化コバルトを含んだシリカゲルは、塩化コバルトの配位水の数による色調変化を利用し、赤紫から青紫に変化する湿度インジケータを兼ねた吸湿剤として非常によく用いられている。しかしながら、このシリカゲルをはじめとした小袋状吸湿剤は、誤飲の問題や、包装の煩雑さなどから、最近の傾向としては出来るだけ小袋状吸湿剤を取除きたいという傾向が見うけられる。また、上記インジケータ機能を有する吸湿剤はコバルト化合物を用いており、安全性という点から改良が望まれている。

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【0009】

これらの問題点を解決する為に、各種容器に吸湿剤を練り込むことで、吸湿性を付与した技術が開発されている。これらの技術はすでに公知の技術である。しかしながら、高含有量の吸湿剤を練り込む課題点として容器の強度物性の低下があげられる。特に代表的な事例として、引用文献1記載のポリマーに吸湿剤を配合した吸湿容器が挙げられる。本引用文献によると、熱可塑性樹脂に吸湿剤およびチャンネル構造形成剤を配合することで、射出成形容器を成形している。機構としては、吸湿剤が選択的にチャンネル構造形成剤からなる相に分散し、その局所的な濃度分布と吸湿を利用して、徐々にチャンネルユニット部分を起点に微細クラックを発生させ、そのクラックを水分の通り道とすることで吸湿性を向上させている。しかしながら、この容器も吸湿能力は有するが、クラックの発生は容器の強度物性への影響が懸念されるところである。

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【0010】

容器物性の改善も吸湿機能を付与した樹脂組成物あるいはそれを用いた積層体、包装体には必須な項目であるが、吸湿機能の持続性と効果の確認という意味では、インジケータ機能は必要な機能である。特に、吸湿剤はその飽和吸湿能力に到達すると、当然の事ながら吸湿機能を発現しない。そのため、内容物の品質の確認を消費者が目視で確認できるという意味でも、インジケータ機能を付与したいところであるが、現状ではインジケータ機能を付与した包装体は確認されていない。

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【0011】

【特許文献1】

米国特許第6, 214, 255号公報

【0012】

【発明が解決しようとする課題】

本発明の課題は上記の実情を考慮したものであり、組成物としての強度物性の改善させながらも、インジケータ機能および吸湿機能を有する事が可能な樹脂組成物およびそれを用いた積層体、包装体を得ることが挙げられる。

【0013】

【課題を解決するための手段】

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本発明は上記課題を克服するために考え出されたものであり、

請求項1記載の発明は、ポリオレフィン樹脂を主成分とし、これらの樹脂100重量部に対し少なくとも吸湿機能を有する無機化合物を1～100重量部含有する樹脂組成物において、吸湿前後における色の変化（色差＝ ΔE ）が少なくとも3以上である事を特徴とする、吸湿機能かつインジケータ機能を有する樹脂組成物、としたものである。

【0014】

請求項2記載の発明は、吸湿機能を有する無機化合物が合成あるいは天然ゼオライトである事を特徴とする、請求項1記載の吸湿機能かつインジケータ機能を有する樹脂組成物、としたものである。

【0015】

請求項3記載の発明は、主成分となるポリオレフィン樹脂が、シクロペンタジエニル誘導体の周期律表第ⅠⅠⅠ、ⅠⅤ、Ⅴ、ⅤⅠ、ⅠⅩ、Ⅹ族遷移金属原子からなる錯体もしくは、上記金属錯体に必要に応じてメチルアルミノキサンからなる、シングルサイト触媒を用いて得られたエチレン- α オレフィン共重合体を必須成分として含むことを特徴とする、請求項1または2記載の吸湿機能かつインジケータ機能を有する樹脂組成物、としたものである。

【0016】

請求項4記載の発明は、請求項1、2、または3記載の樹脂組成物層を設けたことを特徴とする積層体、としたものである。

【0017】

請求項5記載の発明は、請求項1、2、または3記載の樹脂組成物層のどちらか一方に、ポリエチレン、エチレン- α オレフィン共重合体、ポリプロピレン、プロピレン- α オレフィン共重合体、エチレン-環状オレフィン共重合体、アルミ箔、アルミ蒸着フィルム、無機化合物蒸着フィルムなどの防湿層を設けたことを特徴とする請求項4記載の積層体、としたものである。

【0018】

請求項6記載の発明は、請求項4または5記載の積層体から形成された包装体、としたものである。

【0019】

【発明の実施の形態】

以下、本発明を詳細に説明する。本発明の吸湿機能かつインジケータ機能を有する樹脂組成物は、ポリオレフィン樹脂を主成分とし、これらの樹脂100重量部に対し少なくとも吸湿機能を有する無機化合物を1～100重量部含有する樹脂組成物であり、特に、主成分となるポリオレフィン樹脂が、シクロペンタジエニル誘導体の周期律表第ⅠⅠⅠ、ⅠⅤ、Ⅴ、ⅤⅠ、ⅠⅩ、Ⅹ族遷移金属原子からなる錯体もしくは、上記金属錯体に必要に応じてメチルアルミノキサンからなる、シングルサイト触媒を用いて得られたエチレン- α オレフィン共重合体を必須成分として含む事が挙げられる。

【0020】

吸湿機能を付与するという点では、各種吸湿剤を用いる事が可能であるが、インジケータ機能を付与するという点では、合成あるいは天然ゼオライトが好ましい。これらゼオライト系化合物は、吸湿能力が高い事から各種熱可塑性樹脂に配合する検討が行われてきた。ただし、ゼオライト系の吸湿剤を熱可塑性樹脂に配合することで、吸湿に伴い暗褐色に変化するという現象がしばしば確認されている。この内容は、ゼオライトと熱可塑性樹脂からなる組成物は、吸湿により色調変化を伴う事からインジケータとしての機能を果す事が可能であるが、発色が鮮やかな色彩でない事、そして樹脂が劣化した色調に見受けられる事から、この組成物自体を包装体に展開する上で課題が生じた。

【0021】

そこで、この現象に着目し、色調を鮮やかに変色させる事を目的として誠意検討した結果、詳細原理は不明であるが、シクロペンタジエニル誘導体の周期律表第ⅠⅠⅠ、ⅠⅤ、Ⅴ、ⅤⅠ、ⅠⅩ、Ⅹ族遷移金属原子からなる錯体もしくは、上記金属錯体に必要に応じてメ

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チルアルミノキサンからなる、シングルサイト触媒を用いて得られたエチレン- α オレフィン共重合体を必須成分として含むポリオレフィン樹脂中に、上記合成あるいは天然ゼオライトを配合する事で、吸湿後に鮮やかな黄色に変色する事を見出す事が出来た。変色の指標としては、色彩計をもちいることで測定する事が可能であり、吸湿前後における色差(ΔE)が3以上である事が挙げられる。3より少ないと、インジケータとしての明確さにかける。

【0022】

このような触媒の例として、ビス(シクロペンタジエニル)ジルコニウムクロリドにメチルアルミノキサンを加えて得られたシングルサイト触媒(カミンスキー触媒)やその誘導体が挙げられる。金属としては特に、チタニウムやジルコニウムやハフニウムなどの周期律第IV族の遷移金属が用いられるが、特にこれらに限定されるものでない。また、上記触媒は、嵩高い2つのシクロペンタジエニル基に遷移金属が導入された構造を有するが、チタン系の幾何拘束触媒を用いることで、C6、C8、あるいはC9以上の高級 α オレフィンも導入する事が可能である。

【0023】

又、インジケータとしての発色性だけでなく、シングルサイト系触媒を用いる利点は以下の内容が上げられる。

【0024】

- (1) 分子量分布が狭い
- (2) コモノマーの導入位置が制御しやすい。
- (3) ラメラ間に存在するタイ分子が多いため、引裂きなどに対する強度に優れる。
- (4) 柔軟性を付与することが可能
- (5) ストレスクラッキング耐性に優れる

【0025】

さらに、密度が 0.930 g/cm^3 以下、特に密度領域が $0.850\sim 0.925\text{ g/cm}^3$ のものは、ポリオレフィンエラストマーあるいはプラスチックの領域に入り、高含量の無機化合物を配合した樹脂組成物の強度物性という点で非常に好ましい。

【0026】

上記内容は強度物性に関するものであるが、これらポリオレフィンエラストマーあるいはプラスチックの領域を用いる利点としては、熱可塑性樹脂に配合したゼオライトの吸湿速度が挙げられる。ポリオレフィン系樹脂は疎水性であるため、樹脂中に吸湿剤を配合すると吸湿速度を遅くさせてしまう。しかしながら、上記密度範囲のポリオレフィン系樹脂を用いる事で、非晶部分を水分が透過しやすくなり、高結晶性の材料に吸湿剤を配合するよりも吸湿速度を向上させる事が可能である。

【0027】

また、シングルサイト系触媒によるエチレン- α オレフィン共重合体は無機化合物の分散性に優れる。特に上記密度範囲はなお有効である。このような強度物性、柔軟性、無機化合物分散性、吸湿速度と言った点で、本材料系を用いることは非常に好ましい。

【0028】

必要に応じては上記以外の各種添加剤、酸化防止剤、難燃剤、スリッパ剤、アンチブロッキング剤、分散剤など各種添加剤を配合しても構わない。

【0029】

これらの樹脂組成物の製造方法としては、最終製品の成形方法および必要とされる吸湿能力、インジケータとしての発色などの要求機能により設定した各種所定配合量の材料を、リボンミキサー、タンブラーミキサー、ヘンシェルミキサーなどを用いてドライブレンドし、単軸押出機、二軸押出機などの押出機、バンバリーなどの混練機を用いて、融点以上 280°C 以下、好ましくは 260°C 以下、さらに好ましくは 240°C 以下で混練することで得られる。その際、必要に応じて無機系吸湿剤をあらかじめオレフィン系ワックスなどの分散剤で表面処理を施しても構わない。

【0030】

本発明の吸湿能力を有する樹脂組成物は、押出ラミネーション成形、押出キャスト成形、インフレーション成形、インジェクション成形、ダイレクトブロー成形など各種成形法を用いて積層体とすることが可能である。また上述した成形法で得られたフィルム（インフレーションなど）については後工程でドライラミネーションやウェットラミネーション、ノンソルベントラミネーションにより積層体を得ることも可能であり、またインジェクション成形で得られたプリフォームを延伸ブロー成形により多層延伸ブローボトルにすることも可能であるが、これらの成形法に限られるものではない。

【0031】

本発明の樹脂組成物を積層体として用いる場合、樹脂組成物の少なくともどちらか一層は、水分バリア性を有する材料を設けた方が好ましい。これらの材料としては、低密度ポリエチレン、中密度ポリエチレン、高密度ポリエチレン、エチレン- α オレフィン共重合体、ポリプロピレン樹脂、プロピレン- α オレフィン共重合体、エチレン-感情オレフィン共重合体などの各種ポリオレフィン樹脂やポリビニリデンクロライドのようなバリアコート層を設けた基材、アルミ箔、アルミ蒸着フィルム、シリカやアルミナをPVD法あるいはCVD法により各種基材上に蒸着させたバリアフィルムを用いた方が良い。これらのバリア層を用いることで、これらのバリア層を僅かに透過した水分を吸収するだけでなく、包装体のヘッドスペースの湿度を低下させることが可能になる。

【0032】

積層体の例を以下に記載する。積層体の例に記載されている記号は、以下に記載する。

【0033】

A：ポリオレフィン樹脂、B：ポリエステルフィルム、C：ポリビニリデンクロライドコート、D：アルミ箔

【0034】

構成例-1

層構成：A／吸湿能力を有する樹脂組成物

成形法：押出成形、射出成形、ブロー成形、など

用途：シート、中空容器、カップ、トレイなど

【0035】

構成例-2

層構成：B／C／接着剤／A／吸湿能力を有する樹脂組成物

成形法：押出／ドライラミネートなど

用途：軟包装体、蓋材

【0036】

構成例-3

層構成：B／接着剤／D／接着剤／A／吸湿能力を有する樹脂組成物

成形法：押出／ドライラミネートなど

用途：軟包装体、蓋材

【0037】

構成例-4

層構成：紙／A／D／接着剤／A／吸湿能力を有する樹脂組成物

成形法：押出ラミネートなど

用途：複合紙容器など

【0038】

上述したように、様々な構成で得られた積層体は、そのまま各種用途の包装体へ展開することが可能である。これらの例は上述した内容にかぎられないで、様々な包装形態へ展開が可能になる。また、これらの包装形態を組み合わせることで、水分を吸収し、吸湿能力を有する包装体を形成することが可能になる。

【0039】

また、この用途としては特に限定されるものではなく、軟包装体、中空容器、トレイまたはカップ、複合紙容器などに用いる事も可能である。

【0040】

【実施例】

以下に本発明の実施例を示すが、それに限定されるものではない。

【0041】

〔樹脂組成物の作成：材料〕

以下の材料を用いた。

【0042】

＜熱可塑性樹脂＞

・A-1：シングルサイト エチレン-ヘキセン-1共重合体（MI=25、曲げ弾性率80MPa、密度0.901g/cm³）

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・A-2：ホモポリプロピレン（MI=30、曲げ弾性率1750MPa、密度0.900g/cm³）

・A-3：マルチサイト エチレン-オクテン-1共重合体 MI=20、曲げ弾性率420MPa、密度0.925g/cm³）

・A-4：低密度ポリエチレン（MI=20、曲げ弾性率160MPa、密度0.915g/cm³）

【0043】

＜無機化合物＞

・B-1：合成ゼオライト

・B-2：粉末状塩化コバルト含有シリカゲル

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【0044】

〔樹脂組成物の作成：製造〕

あらかじめ、上記熱可塑性樹脂とポリオレフィン系分散材の混合物100重量部に対し、無機化合物を67重量部（重量%として約40wt%）になるように調整した混合物を2軸押出機（φ=30、L/D=49）により吐出9kg、200℃、50rpmでコンパウンドを行った。得られた樹脂組成物は、空冷後ペレタイズを行い、以下に示す成形法に用いた。

【0045】

〔評価サンプルの作成：製造〕

樹脂組成物のインジケータ機能の確認については、2種3層の共押出キャストフィルムを作成する事で評価を行った。層構成はサポート樹脂層／本発明の樹脂組成物層／サポート樹脂層=15μm／50μm／15μmである（加工温度220℃）。この時のサポート樹脂層の選定は、キャスト製膜が可能でかつ、本発明の樹脂組成物層で用いた熱可塑性樹脂との界面接着が良好な材料を用いた。すなわち、ポリエチレンあるいはエチレン-αオレフィン共重合体であればポリエチレン系樹脂を、ポリプロピレン樹脂であれば、ポリプロピレン系樹脂あるいは低結晶性のエチレン-αオレフィン共重合体を用いた。得られた多層フィルムを40℃-90%RH環境下で保存試験を行い、吸湿量に対する色調変化をオリンパス株式会社製色彩計で測定した。

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【0046】

樹脂組成物の吸湿機能の確認については、図1に示すスクリーネジ式中空容器およびインナー容器を別々に射出成形（最外層：ホモポリプロピレン樹脂、最内層：本発明の樹脂組成物）で成形を行ない、後工程で一体化させた容器を用いた。容器形状は、高さ60mm、底面積約1250mm²（75000mm³）の円柱状容器であり、樹脂組成物層の目付けは約8gである。また、外層の容器はホモポリプロピレン樹脂を用いて、目付け10g、厚さは約1.5mmに成形した。この容器を図2に示すように湿度センサーを装填し、容器開封に伴う容器内湿度変化をT&D社製サーモレコーダーで測定した。

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【0047】

また、図1をみてもわかるように、本吸湿容器はキャップとインナー容器が開閉作業を繰り返す事で、インナー容器が変形する事が確認される。これは容器内の密封性を保つためであるが、その開封作業に伴うインナー容器の破壊挙動を、強度物性として評価を行った（

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開閉数 50 回)。

【0048】

[インジケータ機能の確認]

<実施例 1>

A-1、B-1 を用いて得られた樹脂組成物を用い、サポート樹脂層としてメルトインデックスが 4.0 のエチレン- α オレフィン共重合体を用いることで共押出多層フィルムを製膜した。結果を図 3 と図 4 に示す。

【0049】

<実施例 2>

A-1、B-1 を用いて得られた樹脂組成物を用い、さらにこの樹脂をサポート樹脂として用いたエチレン- α オレフィン共重合体で希釈する事で、A-1 と上記エチレン- α オレフィン共重合体の合わせて 100 重量部に対し B-1 が 34 重量部 (重量%として約 20 wt%) になるように、実施例 1 記載の方法で共押出多層フィルムを製膜した。結果を図 3 および図 4 に示す。

【0050】

<比較例 1>

A-4、B-1 を用いた以外は実施例 1 と同じである。

【0051】

<比較例 2>

A-2、B-1 を用い、サポート樹脂としてメルトインデックスが 6.0 のブロックポリプロピレンを用いた以外は実施例 1 と同じである。

【0052】

<比較例 3>

A-1、B-2 を用いた以外は実施例 1 と同じである。

【0053】

<比較例 4>

組成物中の B-1 の割合を 0.5 重量部にした以外は実施例 1 と同じである。

【0054】

図 3 から実施例 1、2、比較例 1～3 は吸湿性を有する無機化合物を配合している為、吸湿機能を有する事が確認されるが、図 4 の色差変化から、実施例 1 は吸湿機能の最終飽和到達時点で $\Delta E > 10$ を超えており、配合比がおよそ半分の実施例 2 でも $\Delta E > 6$ を有する。これらの色は鮮明かつクリアな黄色であり、吸湿により組成物全体が均一に白色状態から鮮明な黄色に変化する事が可能である。

【0055】

また、通常の高密度ポリエチレンを配合した実施例 3 では $\Delta E < 1$ であり、僅かに変色はするが明確さにかける。またポリプロピレン樹脂を配合した場合は $\Delta E > 10$ にはなるが変色が暗褐色であり、インジケータ機能は有するが外観上の問題を伴う。

【0056】

比較例 3 に示すように塩化コバルトを配合したシリカゲルを用いた場合は、 $\Delta E > 15$ で、吸湿により鮮明に青から赤紫に変色するが、配合した無機化合物のみが変色しているため、無機化合物の分散ムラによる濃度ムラがあり、また微視的に見ると、無機化合物自体が変色している為、変色部が粒状に見え、外観不良を伴った。

【0057】

[吸湿機能および強度物性の評価]

<実施例 3>

実施例 1 で用いた樹脂組成物をインナー容器として成形した。その時の 1、10、30、50 回開封作業繰り返した時の、どれだけ湿度の低下が可能かを示す容器内湿度およびインナー容器の破損の状況を容器破損として、以下の比較例 5～7 を併せて表 1 にまとめる。

【0058】

< 比較例 5 >

A-3 を用いて得られた組成物を使用した以外は実施例 3 と同じである。

【 0 0 5 9 】

< 比較例 6 >

比較例 2 で用いた樹脂組成物をインナー容器として成形した以外は実施例 3 と同じである。

【 0 0 6 0 】

< 比較例 7 >

比較例 4 で用いた樹脂組成物をインナー容器として成形した以外は実施例 3 と同じである。

【 0 0 6 1 】

【 表 1 】

	開閉回数					
	1回	10回	30回	50回		
	容器内湿度	容器破損	容器内湿度	容器破損	容器内湿度	容器破損
実施例3	8%RH	無し	8%RH無し	無し	9%RH	無し
比較例5	10%RH	無し	9%RH	クラック発生⇒中止		
比較例6	8%RH	無し	10%RH	無し	9%RH⇒中止	
比較例7	70%RH	無し	82%RH	無し	85%RH	無し

【 0 0 6 2 】

実施例 3 および比較例 5 ～ 7 に示すように、樹脂組成物としては吸湿機能を有する為、容器内の湿度を低湿度で維持する事が可能である。また、実施例 3 では、上述してきたように鮮明な黄色に変色する事からインジケータ機能を有する事も確認されている。一方、強度物性という点でもシングルサイト系エチレンーαオレフィン共重合体の効果が得られており、特にポリオレフィンプラスチック領域の材料を用いる事で、インナー容器のクラックの発生を抑制している事が確認されている。また当然の事ながら比較例 7 のように吸湿機能を有する無機化合物の配合量が少ないと、吸湿機能を維持できない。

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【 0 0 6 3 】

【 発明の 効果 】

本発明の結果から、吸湿器能を有しながらも、吸湿により鮮明な色調変化を有する樹脂組成物を得る事が可能である。また、この樹脂組成物を用いた積層体／包装体も吸湿機能だけでなく、インジケータ機能を有する事が可能である事から、従来の小袋状吸湿剤の添加が必要でなく、かつ内容物の品質確認という意味でも非常に有効である。無機化合物として吸湿剤を用いると容器の吸湿性が認められるようになる。また、従来高含有量の無機化合物を配合した樹脂組成物はその強度物性が問題視されていたが、本材料処方を用いる事で改善させる事も可能である。

【 図面の 簡単な説明 】

【 図 1 】 実施例で用いた容器の模式図および開閉に伴う機構である。

【 図 2 】 吸湿機能評価時の容器の形状（センサー導入）の模式図である。

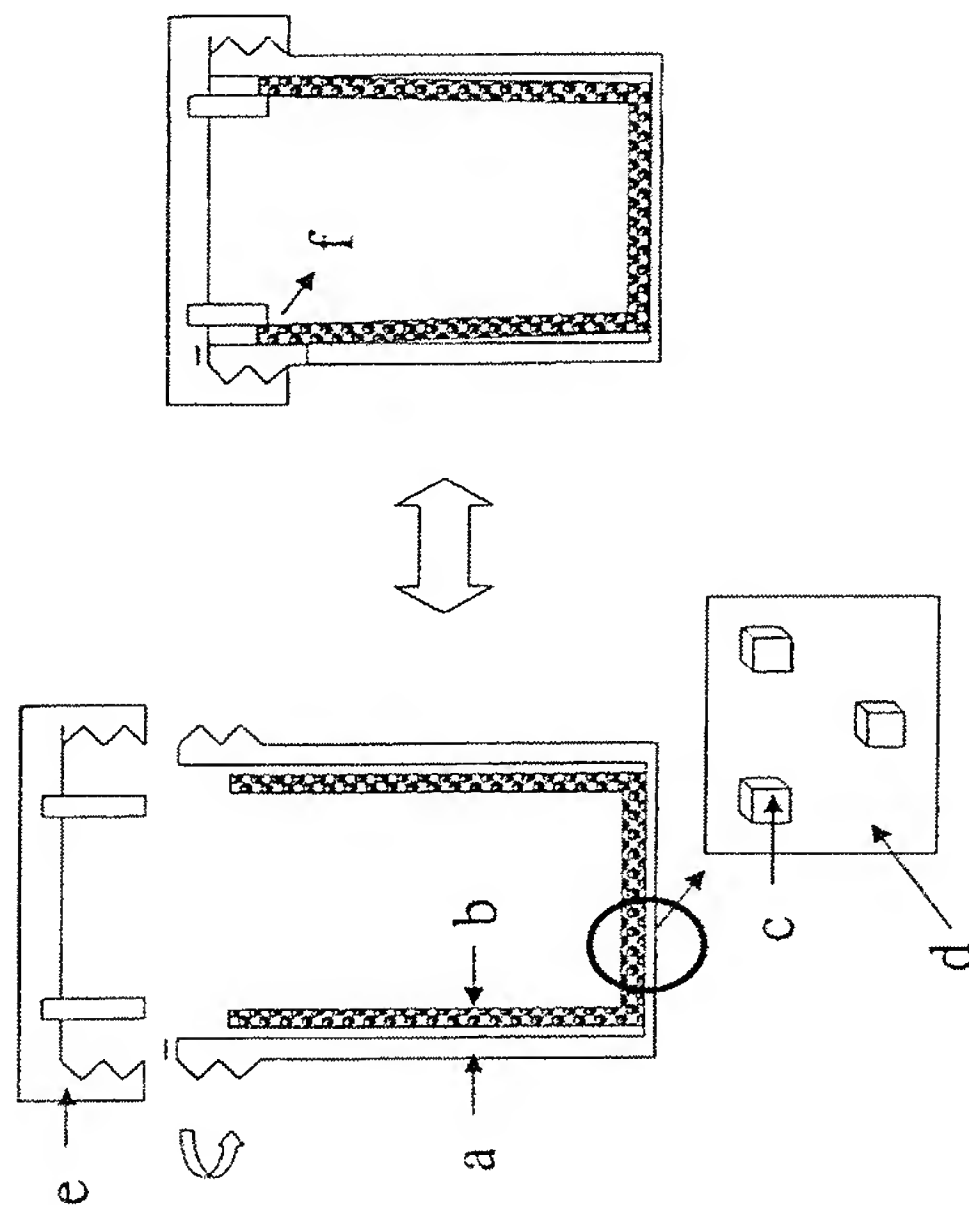
【 図 3 】 実施例、比較例の吸湿挙動を示すグラフである。

【 図 4 】 実施例、比較例の色差変化を示すグラフである。

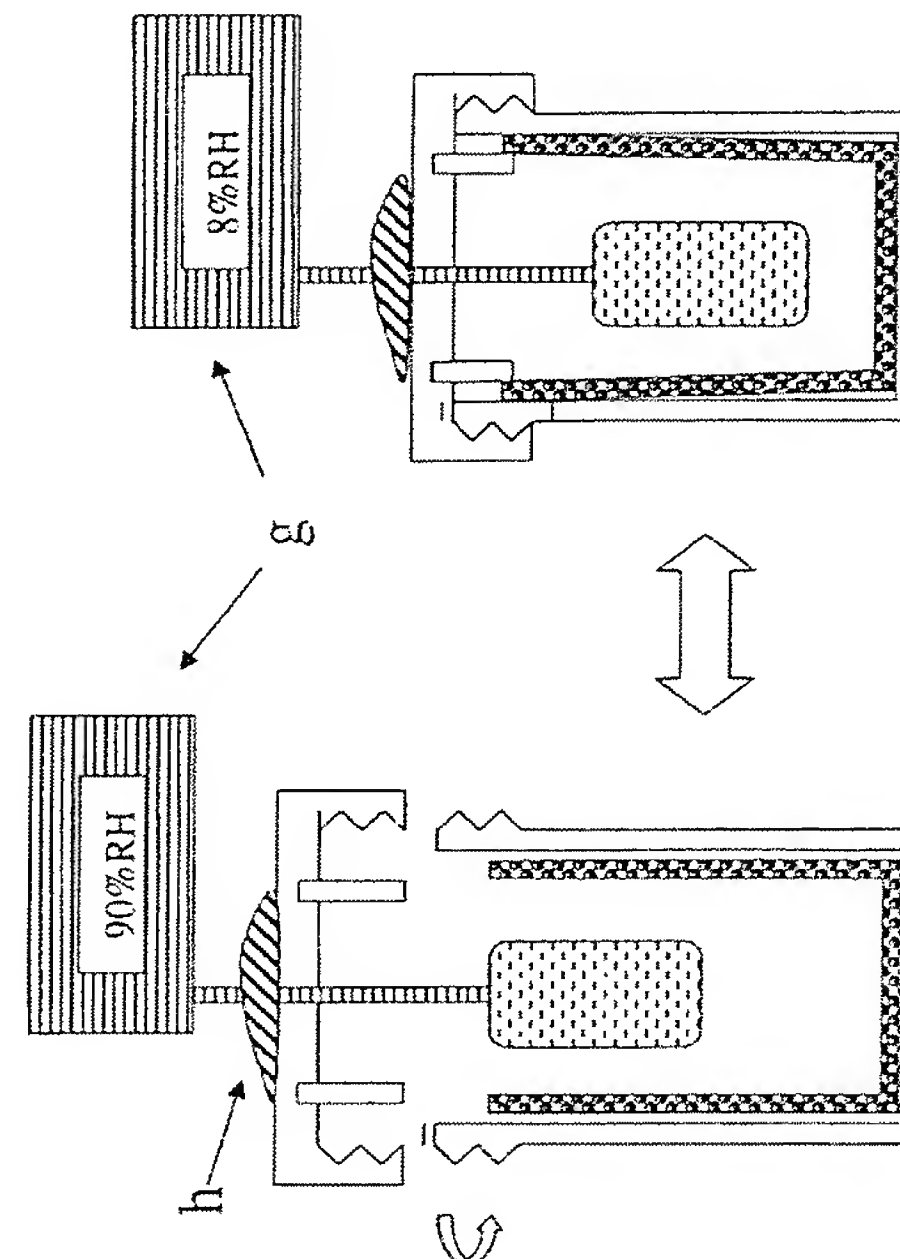
【 符号の説明 】

- a : 中空容器外側
- b : 中空容器内側（インナー容器樹脂組成物層）
- c : 無機化合物
- d : 樹脂 A
- e : キャップ
- f : インナー容器／キャップ密封部分
- g : 湿度センサー
- h : 湿度センサーとキャップを固定するバインダー部

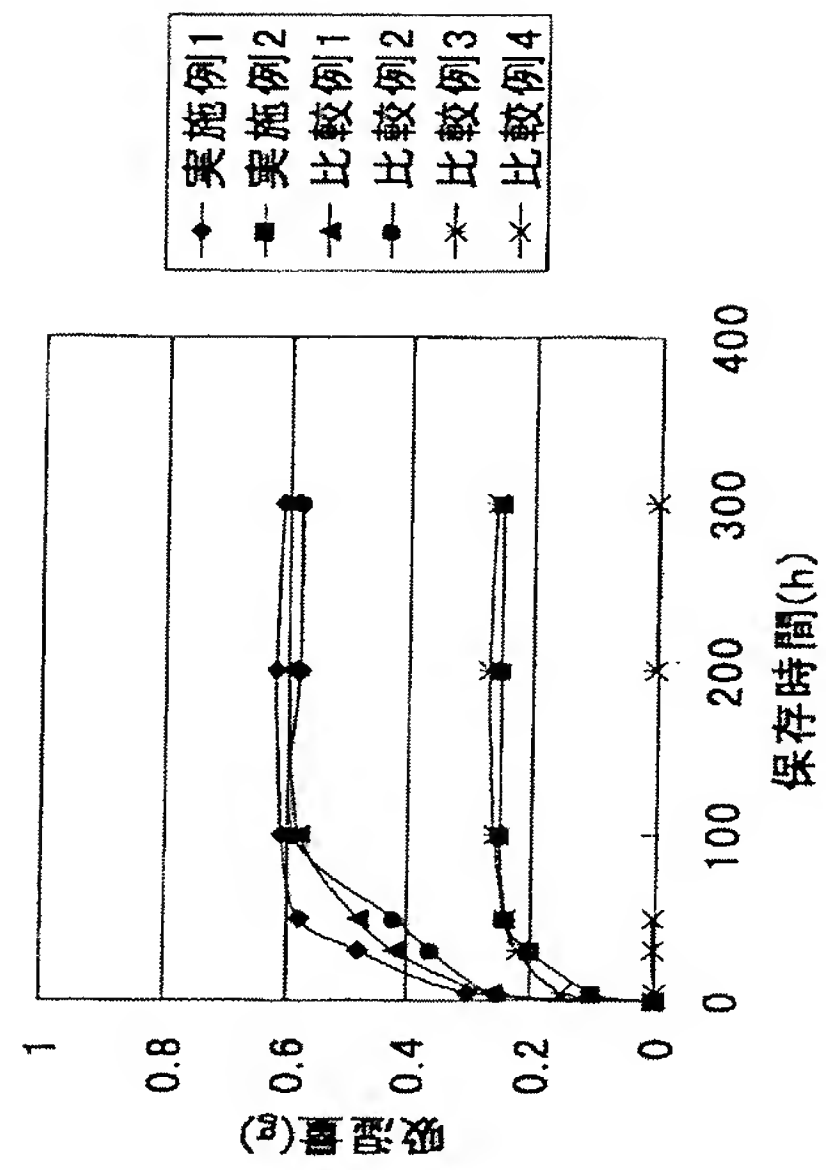
【 図 1 】



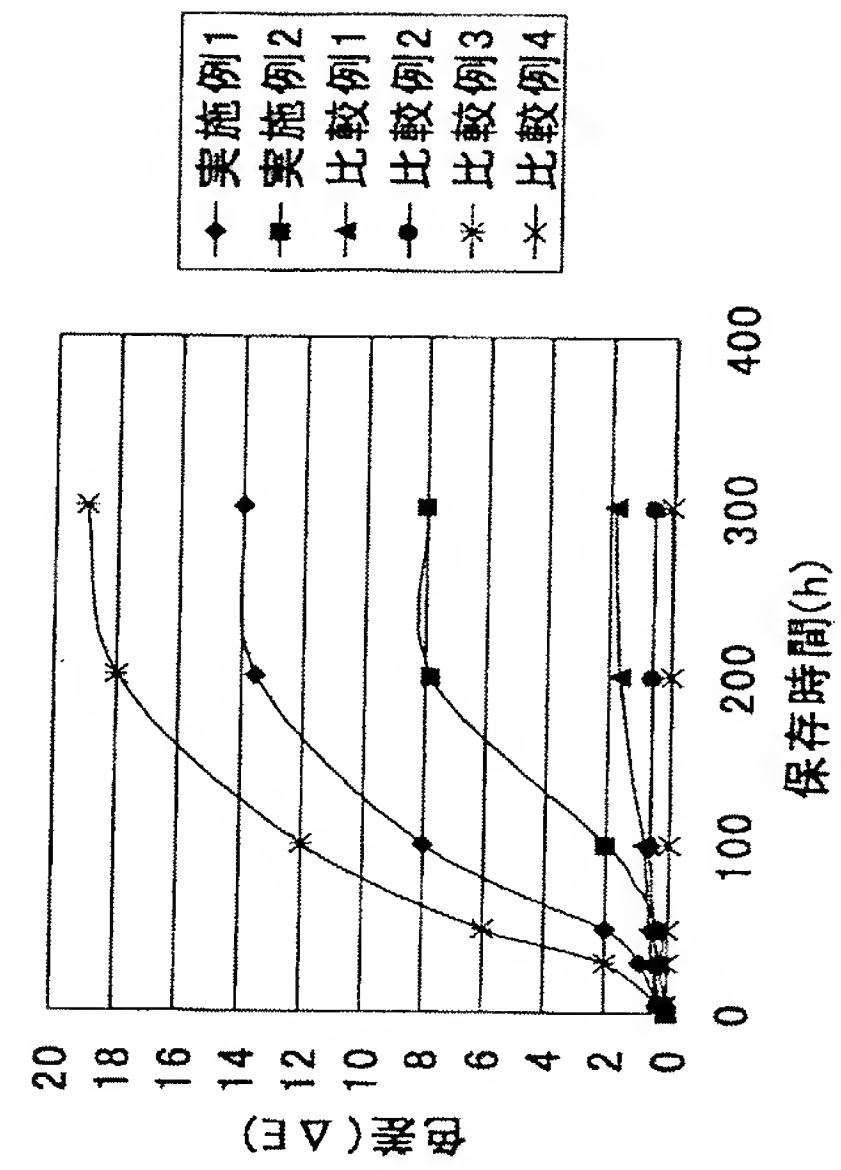
【 図 2 】



【図 3】



【図 4】



フロントページの続き

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4J002 BB031 BB051 BB101 BB121 BB141 BB151 DJ006 FD206 GG02

RESIN COMPOSITION HAVING MOISTURE-ABSORBING FUNCTION AND INDICATOR FUNCTION AND LAMINATE AND PACKAGE EACH USING THE SAME

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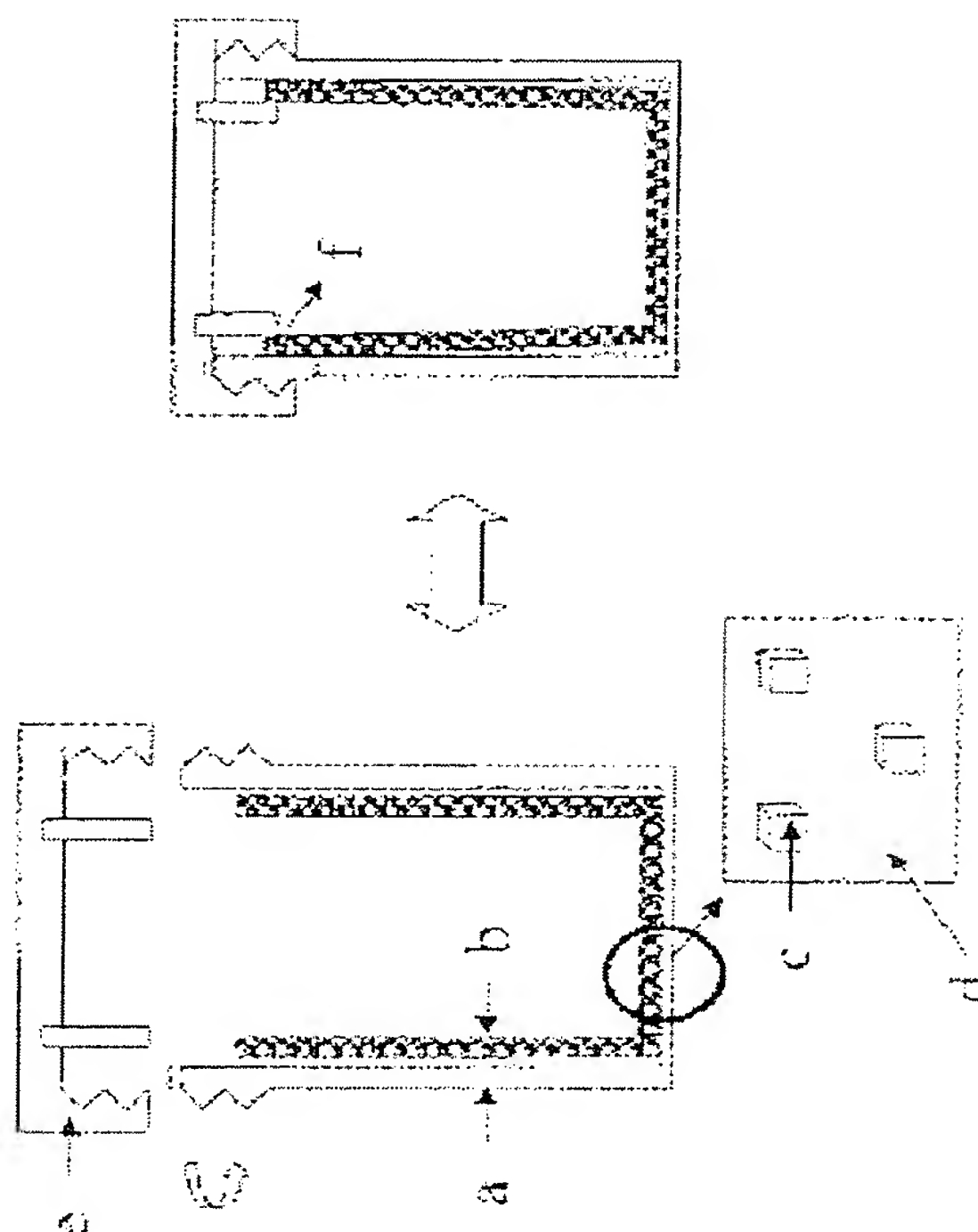
Priority number(s): JP20030131172 20030509

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Abstract of JP2004331855

PROBLEM TO BE SOLVED: To provide a resin composition having an indicator function and a moisture-absorbing function while improving physical properties of strength as a composition and to provide a laminate and a package by using the resin composition.

SOLUTION: The resin composition is obtained by using a polyolefin resin containing, as an essential component, an ethylene-[alpha]-olefin copolymer obtained by using a single site catalyst comprising a metal complex composed of a specific transition metal atom of a cyclopentadienyl derivative and as necessary, methylaluminoxane as a main component and adding 1-100 pts.wt. inorganic compound such as zeolite having at least moisture-absorbing function to 100 pts.wt. of the polyolefin resin. In the resin composition, the change (color difference=[Delta]E) of color before and after moisture absorption is kept to at least ≥ 3 and has the moisture-



absorbing function and the indicator
function.

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CLAIMS

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[Claim(s)]

[Claim 1]

The resin constituent which has the moisture absorption function and indicator function which use polyolefin resin as a principal component, set the inorganic compound which has a moisture absorption function at least to these resin 100 weight sections to the resin constituent which carries out 1-100 weight section content, and are characterized by change (color difference = $\Delta E$ ) of the color before and behind moisture absorption being at least three or more.

[Claim 2]

The resin constituent which has the moisture absorption function according to claim 1 and indicator function which are characterized by the inorganic compound which has a moisture absorption function being composition or natural zeolite.

[Claim 3]

the polyolefin resin used as a principal component -- the [ of a cyclopentadienyl derivative / periodic table ] -- the resin constituent which has the moisture absorption function according to claim 1 or 2 and indicator function which are characterized by including the ethylene-alpha olefine copolymer which turns into a complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom, or the above-mentioned metal complex from methyl aluminoxane if needed, and which was obtained using the single site catalyst as an indispensable component.

[Claim 4]

The layered product characterized by preparing claims 1 and 2 or a resin constituent layer given in three.

[Claim 5]

The layered product according to claim 4 characterized by preparing damp proof courses, such as a polyethylene and ethylene-alpha olefin copolymer, polypropylene, and propylene-alpha olefin copolymer, an ethylene-annular olefine copolymer, aluminum foil, an aluminum vacuum evaporation film, and an inorganic compound vacuum evaporation film, in either claims 1 and 2 or a resin constituent layer given in three.

[Claim 6]

The package object formed from the layered product according to claim 4 or 5.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]

About the layered product and package object using the resin constituent and it which have a moisture absorption function and an indicator function, since coloring of this invention accompanying moisture absorption is still clearer in a detail and its moisture absorption rate is good, it relates to the layered product and package object using the resin constituent which is excellent in moisture absorption capacity; or these resin constituent.

[0002]

[Description of the Prior Art]

In a field called the package enterprise which packs various contents, the following contents are mentioned greatly as contents of a demand of a "package" or "a package."

[0003]

(1) The "display effectiveness", such as grant of purchase consciousness to a consumer, and presentation of danger

(2) "Contents resistance" for a package object not to be invaded by the contents itself with which it was filled up

(3) "Protection of contents" to an external stimulus

It is subdivided further and these contents of a demand are developed to fine demand quality. Among those, protection of the contents from oxygen or moisture is mentioned for capturing the spotlight especially in respect of "protection of contents." Recently especially in each field, such as the food field, the industrial product field, and medicine, the drugs field, importance has come to be attached to the protection nature of the contents to oxygen or moisture. As the background, deterioration of the contents accompanying moisture absorption or hydrolysis is mentioned [ moisture / decomposition of the contents by oxidation, deterioration, and ] about oxygen.

[0004]

Thus, various approaches have been examined in order to prevent deterioration of the contents by oxygen or moisture. It is mentioned that one of them designs the package object using the ingredient which has the oxygen barrier or moisture barrier property. If an example is given in respect of the moisture barrier, the film which gave dampproofing by using polyolefine system resin with dampproofing, or preparing the poly vinylidene chloride system coating layer in these polyolefines, polyester, and polyamide films is the most common.

[0005]

As for the package object using these moisture barrier property base materials, expansion has spread for various applications from the high moisture barrier property. However, since these moisture barrier property base materials use the chlorine-based polymer, they are in the condition that the alternative is examined.

[0006]

Moreover, the needs [ depending on some contents, it may be accompanied by degradation, and ] to remove not only the moisture barrier property from a container outside but the humidity and the moisture in a head space with few humidity and moisture in a head space are coming out.

[0007]

The present condition is packing the desiccant of the shape of a small bag which packed desiccants, such as silica gel and a calcium oxide, from such a background to the wrapping material which is excellent in a nonwoven fabric or moisture permeability in the industrial product fields, such as the contents which dislike moisture absorption to the degree of pole, for example, moisture absorption food, medicine or drugs, and an electronics device, with the contents which dislike these moisture absorption.

[0008]

The silica gel containing especially a cobalt chloride uses the color tone change by the number of the coordinated water of a cobalt chloride, and is used very well as a desiccant which served as the humidity indicator which changes from purplish red to purple-blue. However, the inclination to want to remove a small bag-like desiccant as much as possible as a recent trend can see small bag-like desiccants including this silica gel triggered by the problem of intake by mistake, the complicatedness of a package, etc. Moreover, the desiccant which has the above-mentioned indicator function uses the cobalt compound, and amelioration is desired from the point of safety.

[0009]

In order to solve these troubles, the technique which gave hygroscopicity to various containers by scouring a desiccant is developed. These techniques are already well-known techniques. However, the fall of the physical properties of a container on the strength is raised as a technical-problem point of scouring the desiccant of a high content. As a typical example, the moisture absorption container which blended the desiccant with the polymer of bibliography 1 publication is mentioned especially. According to this bibliography, the injection molded container is fabricated by blending a desiccant and a channel structure formation agent with thermoplastics. As a device, a desiccant distributes to the phase which consists of a channel structure formation agent alternatively, generates a detailed crack with a channel unit part as the starting point gradually using the local concentration distribution and moisture absorption, and is raising hygroscopicity by making the crack into a path as moisture. However, although moisture absorption capacity also has this container, as for generating of a crack, we are just going to be anxious about the effect of the physical properties on the strength on a container.

[0010]

Although it is an item indispensable on the layered product and package object using the resin constituent with which the improvement of container physical properties also gave the moisture absorption function, or it, in the semantics of the durability of a moisture absorption function, and the check of effectiveness, an indicator function is a required function. If especially a desiccant reaches the saturation moisture absorption capacity, it will not discover a moisture absorption function with a natural thing. Therefore, although he wants to give an indicator function also in the semantics that a consumer can check the check of the quality of contents visually, the package object which gave the indicator function is not checked in the present condition.

[0011]

[Patent reference 1]

U.S. Pat. No. 6,214,255 official report

[0012]

[Problem(s) to be Solved by the Invention]

Though the physical properties on the strength as a constituent make the technical problem of this invention improve in consideration of the above-mentioned actual condition, acquiring the layered product using the resin constituent and it which can have an indicator function and a moisture absorption function, and a package object is mentioned.

[0013]

[Means for Solving the Problem]

This invention is invented in order to conquer the above-mentioned technical problem,



Invention according to claim 1 uses polyolefin resin as a principal component, sets the inorganic compound which has a moisture absorption function at least to these resin 100 weight sections to the resin constituent which carries out 1-100 weight section content, and is taken as the resin constituent which has the moisture absorption function and indicator function which are characterized by change (color difference = $\Delta E$ ) of the color before and behind moisture absorption being at least three or more.

[0014]

Invention according to claim 2 is taken as the resin constituent which has the moisture absorption function according to claim 1 and indicator function which are characterized by the inorganic compound which has a moisture absorption function being composition or natural zeolite.

[0015]

the polyolefin resin from which invention according to claim 3 serves as a principal component -- the [ of a cyclopentadienyl derivative / periodic-table ] -- it considers as the resin constituent which has the moisture-absorption function according to claim 1 or 2 and the indicator function which are characterized by to include the ethylene-alpha olefine copolymer which turns into a complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom, or the above-mentioned metal complex from methyl aluminoxane if needed, and which was obtained using the single site catalyst as an indispensable component.

[0016]

Invention according to claim 4 is taken as the layered product characterized by preparing claims 1 and 2 or a resin constituent layer given in three.

[0017]

Invention according to claim 5 is taken as the layered product according to claim 4 characterized by preparing damp proof courses, such as a polyethylene and ethylene-alpha olefin copolymer, polypropylene, and propylene-alpha olefin copolymer, an ethylene-annular olefine copolymer, aluminum foil, an aluminum vacuum evaporatio film, and an inorganic compound vacuum evaporatio film, in either claims 1 and 2 or a resin constituent layer given in three.

[0018]

Invention according to claim 6 is taken as the package object formed from the layered product according to claim 4 or 5.

[0019]

[Embodiment of the Invention]

Hereafter, this invention is explained to a detail. The resin constituent which has the moisture absorption function and indicator function of this invention It is the resin constituent which uses polyolefin resin as a principal component and carries out 1-100 weight section content of the inorganic compound which has a moisture absorption function at least to these resin 100 weight sections. the polyolefin resin which serves as a principal component especially -- the [ of a cyclopentadienyl derivative / periodic table ] -- the complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom -- or It is mentioned that the ethylene-alpha olefine copolymer which turns into the above-mentioned metal complex from methyl aluminoxane if needed and which was obtained using the single site catalyst is included as an indispensable component.

[0020]

Although it is possible to use various desiccants in that a moisture absorption function is given, composition or natural zeolite is desirable at the point of giving an indicator function. Examination to which moisture absorption capacity blends it with various thermoplastics since these zeolites system compound is expensive has been performed. However, the phenomenon of changing to dark brown with moisture absorption is checked by blending the desiccant of a zeolite system with thermoplastics for a while. Since the constituent with which these contents consist of a zeolite and thermoplastics is accompanied by color tone change according to moisture absorption, it can achieve the function as an indicator, but since it saw to that coloring is not skillful color and the color tone to which resin deteriorated, when developing this constituent itself on a package object, the technical problem arose.



[0021]

Then, although the detail principle is unknown as a result of carrying out sincerity examination for the purpose of making a color tone discolor skillfully paying attention to this phenomenon the [ of a cyclopentadienyl derivative / periodic table ] -- the complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom -- or The ethylene-alpha olefine copolymer which turns into the above-mentioned metal complex from methyl aluminoxane if needed and which was obtained using the single site catalyst in the polyolefin resin included as an indispensable component It was able to find out becoming yellow vivid after moisture absorption by blending the above-mentioned composition or natural zeolite. It is possible to measure because it is with a colorimeter as an index of discoloration, and it is mentioned that the color difference before and behind moisture absorption ( $\Delta E$ ) is three or more. If fewer than 3, it will apply to the precision as an indicator.

[0022]

The single site catalyst (Kaminsky catalyst) which added methylamino KISAN to bis(cyclopentadienyl) zirconium chloride, and was acquired as an example of such a catalyst, and its derivative are mentioned. as a metal -- especially -- the [ , such as titanium, a zirconium, and a hafnium, / periodic-law ] -- although IV group's transition metals are used, it is not limited to especially these. moreover, the above-mentioned catalyst -- \*\* -- although it has the structure where transition metals were introduced into two high cyclopentadienyl groups, it is using the geometric restricted catalyst of a titanium system, and it is possible to also introduce C6, C8, or a nine or more C premium grade alpha olefin.

[0023]

Moreover, the contents of not only the color enhancement as an indicator but the following [ advantage / using a single site system catalyst ] are raised.

[0024]

- (1) Molecular weight distribution are narrow.
- (2) It is easy to control the introductory location of a comonomer.
- (3) since there are many Thailand molecules which exist between lamellae -- tearing -- etc. -- excel in the receiving reinforcement.
- (4) It is possible to give flexibility.
- (5) Excel in stress-cracking resistance.

[0025]

Furthermore, the thing of 0.850 - 0.925 g/cm<sup>3</sup> has a very desirable consistency in respect of the physical properties of the resin constituent which 3 or less [ 0.930g //cm ] and a consistency field went into the field of a polyolefine elastomer or a plastomer, and blended the inorganic compound of a high content on the strength.

[0026]

The moisture absorption rate of the zeolite which blended them with thermoplastics as an advantage using the field of these polyolefine elastomer or a plastomer although the above-mentioned contents were \*\*\*\* things at physical properties on the strength is mentioned. Since polyolefine system resin is hydrophobicity, if a desiccant is blended into resin, it will make a moisture absorption rate late. However, it is using the polyolefine system resin of the above-mentioned consistency range, and it is possible to raise a moisture absorption rate rather than moisture becomes easy to penetrate an amorphism part and it blends a desiccant with the ingredient of high crystallinity.

[0027]

Moreover, the ethylene-alpha olefine copolymer by the single site system catalyst is excellent in the dispersibility of an inorganic compound. In addition, especially the above-mentioned consistency range is effective. It is very desirable to use this ingredient system at the point called such physical properties on the strength, flexibility, inorganic compound dispersibility, and moisture absorption rate.

[0028]

If the need is accepted, various additives, such as various additives other than the above, an anti-oxidant, a flame retarder, a slipping agent, an anti blocking agent, and a dispersant, may be blended.

[0029]

The manufacture approach of these resin constituents, the shaping approach of a final product, and the moisture absorption capacity needed, The ingredient of the various predetermined loadings set up by demand functions as an indicator, such as coloring Dryblend is carried out using a ribbon mixer, a tumbler mixer, a Henschel mixer, etc. 260 degrees C or less 280 degrees C or less are preferably obtained by kneading below 240 degrees C still more preferably more than the melting point using kneading machines, such as extruders, such as a single screw extruder and a twin screw extruder, and Banbury. Surface treatment may be beforehand performed for an inorganic system desiccant with dispersants, such as an olefin system wax, if needed in that case.

[0030]

The resin constituent which has the moisture absorption capacity of this invention can be considered as a layered product using the various fabricating methods, such as extrusion lamination shaping, extrusion cast shaping, inflation molding, injection shaping, and direct blow molding. Moreover, although it is also possible to obtain a layered product by the dry lamination, wet lamination, and non solvent lamination at a back process about the films (inflation etc.) obtained by the fabricating method mentioned above and it is also possible to use as a multilayer extension blow bottle preforming obtained with injection shaping by extension blow molding, it is not restricted to these fabricating methods.

[0031]

It is more desirable for one layer of either at least to prepare the ingredient of a resin constituent which has moisture barrier property, when using the resin constituent of this invention as a layered product. It is better to use the base material which prepared a barrier-coating-sealant layer like various polyolefin resin, such as a low-density-polyethylene, medium-density-polyethylene, high-density-polyethylene, and ethylene-alpha olefin copolymer, polypropylene resin, a propylene-alpha olefin copolymer, and an ethylene-feeding olefine copolymer, or poly vinylidene chloride as these ingredients, aluminum foil, an aluminum vacuum evaporation film, and the barrier film that made the silica and the alumina vapor-deposit on [ various ] a base material with PVD or a CVD method. By using these barrier layers, it not only absorbs the moisture which penetrated these barrier layers slightly, but it becomes possible to reduce the humidity of the head space of a package object.

[0032]

The example of a layered product is indicated below. The notation indicated by the example of a layered product is indicated below.

[0033]

A: Polyolefin resin, B:polyester film, C:poly vinylidene chloride coat, D : aluminum foil

[0034]

The example -1 of a configuration

Lamination: The resin constituent which has A / moisture absorption capacity

The fabricating method: Extrusion molding, injection molding, blow molding, etc.

Application: A sheet, a hollow container, a cup, a tray, etc.

[0035]

The example -2 of a configuration

Lamination: The resin constituent which has B/C / adhesives / A / moisture absorption capacity

The fabricating method: Extrusion/dry laminate

Application: A soft package object, lid material

[0036]

The example -3 of a configuration

Lamination: The resin constituent which has B / adhesives / D / adhesives / A / moisture absorption capacity

The fabricating method: Extrusion/dry laminate

Application: A soft package object, lid material

[0037]

The example -4 of a configuration

Lamination: The resin constituent which has paper / A/D / adhesives / A / moisture absorption capacity



The fabricating method: Extrusion lamination etc.

Application: Composite paper container etc.

[0038]

As mentioned above, the layered product obtained with various configurations can be developed to the package object of various applications as it is. Expansion becomes possible to various package gestalten without restricting these examples to the contents mentioned above. Moreover, it becomes possible to form the package object which absorbs moisture and has moisture absorption capacity by combining these package gestalten.

[0039]

Moreover, it is also possible for it not to be limited especially as this application and to use for a soft package object, a hollow container, a tray or a cup, a composite paper container, etc.

[0040]

[Example]

Although the example of this invention is shown below, it is not limited to it.

[0041]

Creation of [resin constituent: Ingredient]

The following ingredients were used.

[0042]

<Thermoplastics>

\*\*A-1: Single site Ethylene-hexene -1 copolymer (MI=25, bending elastic-modulus 80MPa, consistency 0.901 g/cm<sup>3</sup>)

\*\*A-2: Gay polypropylene (MI=30, bending elastic-modulus 1750MPa, consistency 0.900 g/cm<sup>3</sup>)

\*\*A-3: Multi-site Ethylene-octene -1 copolymer MI=20, bending elastic-modulus 420MPa, consistency 0.925 g/cm<sup>3</sup>

\*\*A-4: Low density polyethylene (MI=20, bending elastic-modulus 160MPa, consistency 0.915 g/cm<sup>3</sup>)

[0043]

<Inorganic compound>

\*\*B-1: Permutite

\*\*B-2: Powdered cobalt chloride content silica gel

[0044]

Creation of [resin constituent: Manufacture]

The biaxial extruder ( $\phi=30$ , ratio-of-length-to-diameter=49) performed the compound for the mixture which adjusted the inorganic compound beforehand to the mixture 100 weight section of the above-mentioned thermoplastics and polyolefine system distribution material so that it might become 67 weight sections (considering as % of the weight about 40 wt(s)%) by 9kg of regurgitation, 200 degrees C, and 50rpm. The obtained resin constituent performed pelletizing after air cooling, and used it for the fabricating method shown below.

[0045]

Creation of [evaluation sample: Manufacture]

Creating the two-sort co-extrusion cast film of three layers estimated the check of the indicator function of a resin constituent. Lamination is the resin constituent layer / support resin layer =15micrometer of a support resin layer / this invention / 50 micrometers / 15 micrometers (working temperature of 220 degrees C). Cast film production was possible for selection of the support resin layer at this time, and interface adhesion with the thermoplastics used in the resin constituent layer of this invention used the good ingredient. That is, when it was a polyethylene or ethylene-alpha olefin copolymer and was polypropylene resin about polyethylene system resin, the polypropylene resin or the ethylene-alpha olefine copolymer of low crystallinity was used. The retention test was performed for the obtained multilayer film under the 40 degree-C-90%RH environment, and the color tone change to the amount of moisture absorption was measured with the Olympus, Inc. colorimeter.

[0046]

About the check of the moisture absorption function of a resin constituent, the container which it

fabricated [ container ] with injection molding (the outermost layer: gay polypropylene resin, resin constituent of innermost layer:this invention) separately, and made the screw screw type hollow container and inner container which are shown in drawing 1 unify at a back process was used. A container configuration is the cylindrical container of 2 (75000mm<sup>3</sup>) height of 60mm, and the area of base of about 1250mm, and the superintendent officer of a resin constituent layer is about 8g. Moreover, 10g of superintendent officers and thickness fabricated the container of an outer layer to about 1.5mm using the gay polypropylene resin knot. This container was loaded with the humidity sensor as shown in drawing 2 , and the sir made from T&D also measured the humidity in a container accompanying container opening by the recorder.

[0047]

Moreover, this moisture absorption container is that a cap and an inner container repeat a closing motion activity, and it is checked that an inner container deforms so that it may understand, even if it sees drawing 1 . Although this was for maintaining the sealing performance in a container, it evaluated considering the destructive behavior of the inner container accompanying the opening activity as physical properties on the strength (the number of closing motion 50 times).

[0048]

[A check of an indicator function]

<Example 1>

Using the resin constituent obtained using A-1 and B-1, the co-extrusion multilayer film was produced because a melt index uses the ethylene-alpha olefine copolymer of 4.0 as a support resin layer. A result is shown in drawing 3 and drawing 4 .

[0049]

<Example 2>

The co-extrusion multilayer film was produced by the approach of example 1 publication so that B-1 might become 34 weight sections (about 20 wt(s)% as % of the weight) to the 100 in all weight section of A-1 and the above-mentioned ethylene-alpha olefine copolymer using the resin constituent obtained using A-1 and B-1 by diluting with the ethylene-alpha olefin copolymer using this resin as support resin further. A result is shown in drawing 3 and drawing 4 .

[0050]

<The example 1 of a comparison>

It is the same as an example 1 except having used A-4 and B-1.

[0051]

<The example 2 of a comparison>

Except that the melt index used the block polypropylene of 6.0 as support resin using A-2 and B-1, it is the same as an example 1.

[0052]

<The example 3 of a comparison>

It is the same as an example 1 except having used A-1 and B-2.

[0053]

<The example 4 of a comparison>

It is the same as an example 1 except having made the rate of B-1 in a constituent into the 0.5 weight section.

[0054]

Although having a moisture absorption function is checked since examples 1 and 2 and the examples 1-3 of a comparison have blended the inorganic compound which has hygroscopicity also from drawing 3 , from color difference change of drawing 4 , it is an example 1 at the last saturation attainment time of a moisture absorption function, it is over  $\Delta E > 10$ , and a compounding ratio has  $\Delta E > 6$  also in the half example 2 about. These colors are clear and clear yellow, and can be changed with moisture absorption from a white condition to homogeneity by the whole constituent at clear yellow.

[0055]

Moreover, in the example 3 which blended usual low density polyethylene, it is  $\Delta E < 1$ , and slightly,



although discoloration is carried out, it is applied to precision. Moreover, although it is set to  $\Delta E > 10$  when polypropylene resin is blended, discoloration is dark brown, and although it has an indicator function, it is accompanied by the exterior problem.

[0056]

As shown in the example 3 of a comparison, when the silica gel which blended the cobalt chloride was used, it is  $\Delta E > 15$  and became purplish red from blue vividly according to moisture absorption, but since only the blended inorganic compound has discolored, if there was concentration nonuniformity by the distributed nonuniformity of an inorganic compound and it saw microscopically, since the inorganic compound itself would have discolored, the discoloration section looked granular and was accompanied by the poor appearance.

[0057]

[A moisture absorption function and evaluation of physical properties on the strength]

<Example 3>

The resin constituent used in the example 1 was fabricated as an inner container. By considering the situation of breakage of the humidity in a container and the inner container in which it is shown whether the fall of humidity is possible as container breakage, 1 at that time, 10, and which when repeating \*\*\*\*\* business 30 or 50 times combine the following examples 5-7 of a comparison, and summarizes them in Table 1.

[0058]

<The example 5 of a comparison>

It is the same as an example 3 except having used the constituent obtained using A-3.

[0059]

<The example 6 of a comparison>

It is the same as an example 3 except having fabricated the resin constituent used in the example 2 of a comparison as an inner container.

[0060]

<The example 7 of a comparison>

It is the same as an example 3 except having fabricated the resin constituent used in the example 4 of a comparison as an inner container.

[0061]

[Table 1]

|      | 開閉数   |      |        |           |       |      |
|------|-------|------|--------|-----------|-------|------|
|      | 1回    | 10回  | 30回    | 50回       |       |      |
|      | 容器内湿度 | 容器破損 | 容器内湿度  | 容器破損      | 容器内湿度 | 容器破損 |
| 実施例3 | 8%RH  | 無し   | 8%RH無し | 無し        | 9%RH  | 無し   |
| 比較例5 | 10%RH | 無し   | 9%RH   | クラック発生⇒中止 |       |      |
| 比較例6 | 8%RH  | 無し   | 10%RH  | 無し        | ⇒中止   |      |
| 比較例7 | 70%RH | 無し   | 82%RH  | 無し        | 85%RH | 無し   |

[0062]

Since it has a moisture absorption function as a resin constituent as shown in an example 3 and the examples 5-7 of a comparison, it is possible to maintain the humidity in a container with low humidity. Moreover, in the example 3, since it becomes clear yellow as mentioned above, having an indicator function is also checked. On the other hand, the effectiveness of a single site system ethylene-alpha olefine copolymer is acquired also in respect of physical properties on the strength, and having controlled generating of the crack of an inner container is checked by using the ingredient of a polyolefine plastomer field especially. Moreover, if there are few loadings of the inorganic compound which has a moisture absorption function like the example 7 of a comparison with a natural thing, a moisture absorption function is unmaintainable.

[0063]

[Effect of the Invention]

It is possible to obtain the resin constituent which has a clear color tone change according to moisture absorption from the result of this invention, though it has moisture absorption \*\*\*\*. Moreover, the small bag-like desiccant of the former [ be / having not only a moisture absorption function but an indicator function / possible ] does not need to be added, and, also as for the layered product / package object using this resin constituent, it is very effective also in the semantics of the quality assurance of contents. The hygroscopicity of a container will come to be accepted if a desiccant is used as an inorganic compound. Moreover, although the physical properties on the strength were regarded as questionable, as for the resin constituent which blended the inorganic compound of a quantity content conventionally, it is possible to also make it improve by using this ingredient formula.

[Brief Description of the Drawings]

[Drawing 1] They are the mimetic diagram of the container used in the example, and a device accompanying closing motion.

[Drawing 2] It is the mimetic diagram of the configuration (sensor installation) of the container at the time of moisture absorption functional evaluation.

[Drawing 3] It is the graph which shows the moisture absorption behavior of an example and the example of a comparison.

[Drawing 4] It is the graph which shows color difference change of an example and the example of a comparison.

[Description of Notations]

a: Hollow container outside

b: Hollow container inside (inner container resin constituent layer)

c: Inorganic compound

d: Resin A

e: Cap

f: An inner container / cap seal part

g: Humidity sensor

h: The binder section which fixes a humidity sensor and a cap

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[Translation done.]

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TECHNICAL FIELD

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[Field of the Invention]

About the layered product and package object using the resin constituent and it which have a moisture absorption function and an indicator function, since coloring of this invention accompanying moisture absorption is still clearer in a detail and its moisture absorption rate is good, it relates to the layered product and package object using the resin constituent which is excellent in moisture absorption capacity, or these resin constituent.

[0002]

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PRIOR ART

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[Description of the Prior Art]

In a field called the package enterprise which packs various contents, the following contents are mentioned greatly as contents of a demand of a "package" or "a package."

[0003]

- (1) It was called the grant of purchase consciousness to a consumer, and presentation of danger.
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[Translation done.]



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## EFFECT OF THE INVENTION

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"The display effectiveness"

(2) "Contents resistance" for a package object not to be invaded by the contents itself with which it was filled up

(3) "Protection of contents" to an external stimulus

It is subdivided further and these contents of a demand are developed to fine demand quality. Among those, protection of the contents from oxygen or moisture is mentioned for capturing the spotlight especially in respect of "protection of contents." Recently especially in each field, such as the food field, the industrial product field, and medicine, the drugs field, importance has come to be attached to the protection nature of the contents to oxygen or moisture. As the background, deterioration of the contents accompanying moisture absorption or hydrolysis is mentioned [ moisture / decomposition of the contents by oxidation, deterioration, and ] about oxygen.

[0004]

Thus, various approaches have been examined in order to prevent deterioration of the contents by oxygen or moisture. It is mentioned that one of them designs the package object using the ingredient which has the oxygen barrier or moisture barrier property. If an example is given in respect of the moisture barrier, the film which gave dampproofing by using polyolefine system resin with dampproofing, or preparing the poly vinylidene chloride system coating layer in these polyolefines, polyester, and polyamide films is the most common.

[0005]

As for the package object using these moisture barrier property base materials, expansion has spread for various applications from the high moisture barrier property. However, since these moisture barrier property base materials use the chlorine-based polymer, they are in the condition that the alternative is examined.

[0006]

Moreover, the needs [ depending on some contents, it may be accompanied by degradation, and ] to remove not only the moisture barrier property from a container outside but the humidity and the moisture in a head space with few humidity and moisture in a head space are coming out.

[0007]

The present condition is packing the desiccant of the shape of a small bag which packed desiccants, such as silica gel and a calcium oxide, from such a background to the wrapping material which is excellent in a nonwoven fabric or moisture permeability in the industrial product fields, such as the contents which dislike moisture absorption to the degree of pole, for example, moisture absorption food, medicine or drugs, and an electronics device, with the contents which dislike these moisture absorption.

[0008]

The silica gel containing especially a cobalt chloride uses the color tone change by the number of the coordinated water of a cobalt chloride, and is used very well as a desiccant which served as the humidity indicator which changes from purplish red to purple-blue. However, the inclination to want to remove a small bag-like desiccant as much as possible as a recent trend can see small bag-like desiccants

including this silica gel triggered by the problem of intake by mistake, the complicatedness of a package, etc. Moreover, the desiccant which has the above-mentioned indicator function uses the cobalt compound, and amelioration is desired from the point of safety.

[0009]

In order to solve these troubles, the technique which gave hygroscopicity to various containers by scouring a desiccant is developed. These techniques are already well-known techniques. However, the fall of the physical properties of a container on the strength is raised as a technical-problem point of scouring the desiccant of a high content. As a typical example, the moisture absorption container which blended the desiccant with the polymer of bibliography 1 publication is mentioned especially.

According to this bibliography, the injection molded container is fabricated by blending a desiccant and a channel structure formation agent with thermoplastics. As a device, a desiccant distributes to the phase which consists of a channel structure formation agent alternatively, generates a detailed crack with a channel unit part as the starting point gradually using the local concentration distribution and moisture absorption, and is raising hygroscopicity by making the crack into a path as moisture. However, although moisture absorption capacity also has this container, as for generating of a crack, we are just going to be anxious about the effect of the physical properties on the strength on a container.

[0010]

Although it is an item indispensable on the layered product and package object using the resin constituent with which the improvement of container physical properties also gave the moisture absorption function, or it, in the semantics of the durability of a moisture absorption function, and the check of effectiveness, an indicator function is a required function. If especially a desiccant reaches the saturation moisture absorption capacity, it will not discover a moisture absorption function with a natural thing. Therefore, although he wants to give an indicator function also in the semantics that a consumer can check the check of the quality of contents visually, the package object which gave the indicator function is not checked in the present condition.

[0011]

[Patent reference 1]

U.S. Pat. No. 6,214,255 official report

[0012]

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]

Though the physical properties on the strength as a constituent make the technical problem of this invention improve in consideration of the above-mentioned actual condition, acquiring the layered product using the resin constituent and it which can have an indicator function and a moisture absorption function, and a package object is mentioned.

[0013]

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MEANS

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[Means for Solving the Problem]

This invention is invented in order to conquer the above-mentioned technical problem, Invention according to claim 1 uses polyolefin resin as a principal component, sets the inorganic compound which has a moisture absorption function at least to these resin 100 weight sections to the resin constituent which carries out 1-100 weight section content, and is taken as the resin constituent which has the moisture absorption function and indicator function which are characterized by change (color difference =  $\Delta E$ ) of the color before and behind moisture absorption being at least three or more.

[0014]

Invention according to claim 2 is taken as the resin constituent which has the moisture absorption function according to claim 1 and indicator function which are characterized by the inorganic compound which has a moisture absorption function being composition or natural zeolite.

[0015]

the polyolefin resin from which invention according to claim 3 serves as a principal component -- the [ of a cyclopentadienyl derivative / periodic-table ] -- it considers as the resin constituent which has the moisture-absorption function according to claim 1 or 2 and the indicator function which are characterized by to include the ethylene-alpha olefine copolymer which turns into a complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom, or the above-mentioned metal complex from methyl aluminosilane if needed, and which was obtained using the single site catalyst as an indispensable component.

[0016]

Invention according to claim 4 is taken as the layered product characterized by preparing claims 1 and 2 or a resin constituent layer given in three.

[0017]

Invention according to claim 5 is taken as the layered product according to claim 4 characterized by preparing damp proof courses, such as a polyethylene and ethylene-alpha olefin copolymer, polypropylene, and propylene-alpha olefin copolymer, an ethylene-annular olefine copolymer, aluminum foil, an aluminum vacuum evaporation film, and an inorganic compound vacuum evaporation film, in either claims 1 and 2 or a resin constituent layer given in three.

[0018]

Invention according to claim 6 is taken as the package object formed from the layered product according to claim 4 or 5.

[0019]

[Embodiment of the Invention]

Hereafter, this invention is explained to a detail. The resin constituent which has the moisture absorption function and indicator function of this invention It is the resin constituent which uses polyolefin resin as a principal component and carries out 1-100 weight section content of the inorganic compound which has a moisture absorption function at least to these resin 100 weight sections. the polyolefin resin which

serves as a principal component especially -- the [ of a cyclopentadienyl derivative / periodic table ] -- the complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom -- or It is mentioned that the ethylene-alpha olefine copolymer which turns into the above-mentioned metal complex from methyl aluminoxane if needed and which was obtained using the single site catalyst is included as an indispensable component.

[0020]

Although it is possible to use various desiccants in that a moisture absorption function is given, composition or natural zeolite is desirable at the point of giving an indicator function. Examination to which moisture absorption capacity blends it with various thermoplastics since these zeolites system compound is expensive has been performed. However, the phenomenon of changing to dark brown with moisture absorption is checked by blending the desiccant of a zeolite system with thermoplastics for a while. Since the constituent with which these contents consist of a zeolite and thermoplastics is accompanied by color tone change according to moisture absorption, it can achieve the function as an indicator, but since it saw to that coloring is not skillful color and the color tone to which resin deteriorated, when developing this constituent itself on a package object, the technical problem arose.

[0021]

Then, although the detail principle is unknown as a result of carrying out sincerity examination for the purpose of making a color tone discolor skillfully paying attention to this phenomenon the [ of a cyclopentadienyl derivative / periodic table ] -- the complex which consists of III, IV, V, VI, IX, and an X group transition-metals atom -- or The ethylene-alpha olefine copolymer which turns into the above-mentioned metal complex from methyl aluminoxane if needed and which was obtained using the single site catalyst in the polyolefin resin included as an indispensable component It was able to find out becoming yellow vivid after moisture absorption by blending the above-mentioned composition or natural zeolite. It is possible to measure because it is with a colorimeter as an index of discoloration, and it is mentioned that the color difference before and behind moisture absorption ( $\Delta E$ ) is three or more. If fewer than 3, it will apply to the precision as an indicator.

[0022]

The single site catalyst (Kaminsky catalyst) which added methylamino KISAN to bis(cyclopentadienyl) zirconium chloride, and was acquired as an example of such a catalyst, and its derivative are mentioned. as a metal -- especially -- the [ , such as titanium, a zirconium, and a hafnium, / periodic-law ] -- although IV group's transition metals are used, it is not limited to especially these. moreover, the above-mentioned catalyst -- \*\* -- although it has the structure where transition metals were introduced into two high cyclopentadienyl groups, it is using the geometric restricted catalyst of a titanium system, and it is possible to also introduce C6, C8, or a nine or more C premium grade alpha olefin.

[0023]

Moreover, the contents of not only the color enhancement as an indicator but the following [ advantage / using a single site system catalyst ] are raised.

[0024]

- (1) Molecular weight distribution are narrow.
- (2) It is easy to control the introductory location of a comonomer.
- (3) since there are many Thailand molecules which exist between lamellae -- tearing -- etc. -- excel in the receiving reinforcement.
- (4) It is possible to give flexibility.
- (5) Excel in stress-cracking resistance.

[0025]

Furthermore, the thing of 0.850 - 0.925 g/cm<sup>3</sup> has a very desirable consistency in respect of the physical properties of the resin constituent which 3 or less [ 0.930g //cm ] and a consistency field went into the field of a polyolefine elastomer or a plastomer, and blended the inorganic compound of a high content on the strength.

[0026]

The moisture absorption rate of the zeolite which blended them with thermoplastics as an advantage



using the field of these polyolefine elastomer or a plastomer although the above-mentioned contents were \*\*\*\* things at physical properties on the strength is mentioned. Since polyolefine system resin is hydrophobicity, if a desiccant is blended into resin, it will make a moisture absorption rate late.

However, it is using the polyolefine system resin of the above-mentioned consistency range, and it is possible to raise a moisture absorption rate rather than moisture becomes easy to penetrate an amorphism part and it blends a desiccant with the ingredient of high crystallinity.

[0027]

Moreover, the ethylene-alpha olefine copolymer by the single site system catalyst is excellent in the dispersibility of an inorganic compound. In addition, especially the above-mentioned consistency range is effective. It is very desirable to use this ingredient system at the point called such physical properties on the strength, flexibility, inorganic compound dispersibility, and moisture absorption rate.

[0028]

If the need is accepted, various additives, such as various additives other than the above, an anti-oxidant, a flame retarder, a slipping agent, an anti blocking agent, and a dispersant, may be blended.

[0029]

The manufacture approach of these resin constituents, the shaping approach of a final product, and the moisture absorption capacity needed, The ingredient of the various predetermined loadings set up by demand functions as an indicator, such as coloring Dryblend is carried out using a ribbon mixer, a tumbler mixer, a Henschel mixer, etc. 260 degrees C or less 280 degrees C or less are preferably obtained by kneading below 240 degrees C still more preferably more than the melting point using kneading machines, such as extruders, such as a single screw extruder and a twin screw extruder, and Banbury. Surface treatment may be beforehand performed for an inorganic system desiccant with dispersants, such as an olefin system wax, if needed in that case.

[0030]

The resin constituent which has the moisture absorption capacity of this invention can be considered as a layered product using the various fabricating methods, such as extrusion lamination shaping, extrusion cast shaping, inflation molding, injection shaping, and direct blow molding. Moreover, although it is also possible to obtain a layered product by the dry lamination, wet lamination, and non solvent lamination at a back process about the films (inflation etc.) obtained by the fabricating method mentioned above and it is also possible to use as a multilayer extension blow bottle preforming obtained with injection shaping by extension blow molding, it is not restricted to these fabricating methods.

[0031]

It is more desirable for one layer of either at least to prepare the ingredient of a resin constituent which has moisture barrier property, when using the resin constituent of this invention as a layered product. It is better to use the base material which prepared a barrier-coating-sealant layer like various polyolefin resin, such as a low-density-polyethylene, medium-density-polyethylene, high-density-polyethylene, and ethylene-alpha olefin copolymer, polypropylene resin, a propylene-alpha olefin copolymer, and an ethylene-feeding olefine copolymer, or poly vinylidene chloride as these ingredients, aluminum foil, an aluminum vacuum evaporation film, and the barrier film that made the silica and the alumina vapor-deposit on [ various ] a base material with PVD or a CVD method. By using these barrier layers, it not only absorbs the moisture which penetrated these barrier layers slightly, but it becomes possible to reduce the humidity of the head space of a package object.

[0032]

The example of a layered product is indicated below. The notation indicated by the example of a layered product is indicated below.

[0033]

A: Polyolefin resin, B: polyester film, C: poly vinylidene chloride coat, D : aluminum foil

[0034]

The example -1 of a configuration

Lamination: The resin constituent which has A / moisture absorption capacity

The fabricating method: Extrusion molding, injection molding, blow molding, etc.

Application: A sheet, a hollow container, a cup, a tray, etc.

[0035]

The example -2 of a configuration

Lamination: The resin constituent which has B/C / adhesives / A / moisture absorption capacity

The fabricating method: Extrusion/dry laminate

Application: A soft package object, lid material

[0036]

The example -3 of a configuration

Lamination: The resin constituent which has B / adhesives / D / adhesives / A / moisture absorption capacity

The fabricating method: Extrusion/dry laminate

Application: A soft package object, lid material

[0037]

The example -4 of a configuration

Lamination: The resin constituent which has paper / A/D / adhesives / A / moisture absorption capacity

The fabricating method: Extrusion lamination etc.

Application: Composite paper container etc.

[0038]

As mentioned above, the layered product obtained with various configurations can be developed to the package object of various applications as it is. Expansion becomes possible to various package gestalten without restricting these examples to the contents mentioned above. Moreover, it becomes possible to form the package object which absorbs moisture and has moisture absorption capacity by combining these package gestalten.

[0039]

Moreover, it is also possible for it not to be limited especially as this application and to use for a soft package object, a hollow container, a tray or a cup, a composite paper container, etc.

[0040]

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[Translation done.]

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EXAMPLE

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[Example]

Although the example of this invention is shown below, it is not limited to it.

[0041]

Creation of [resin constituent: Ingredient]

The following ingredients were used.

[0042]

<Thermoplastics>

\*\*A-1: Single site Ethylene-hexene -1 copolymer (MI=25, bending elastic-modulus 80MPa, consistency 0.901 g/cm<sup>3</sup>)

\*\*A-2: Gay polypropylene (MI=30, bending elastic-modulus 1750MPa, consistency 0.900 g/cm<sup>3</sup>)

\*\*A-3: Multi-site Ethylene-octene -1 copolymer MI=20, bending elastic-modulus 420MPa, consistency 0.925 g/cm<sup>3</sup>

\*\*A-4: Low density polyethylene (MI=20, bending elastic-modulus 160MPa, consistency 0.915 g/cm<sup>3</sup>)

[0043]

<Inorganic compound>

\*\*B-1: Permutite

\*\*B-2: Powdered cobalt chloride content silica gel

[0044]

Creation of [resin constituent: Manufacture]

The biaxial extruder ( $\phi=30$ , ratio-of-length-to-diameter=49) performed the compound for the mixture which adjusted the inorganic compound beforehand to the mixture 100 weight section of the above-mentioned thermoplastics and polyolefine system distribution material so that it might become 67 weight sections (considering as % of the weight about 40 wt(s)%) by 9kg of regurgitation, 200 degrees C, and 50rpm. The obtained resin constituent performed pelletizing after air cooling, and used it for the fabricating method shown below.

[0045]

Creation of [evaluation sample: Manufacture]

Creating the two-sort co-extrusion cast film of three layers estimated the check of the indicator function of a resin constituent. Lamination is the resin constituent layer / support resin layer = 15micrometer of a support resin layer / this invention / 50 micrometers / 15 micrometers (working temperature of 220 degrees C). Cast film production was possible for selection of the support resin layer at this time, and interface adhesion with the thermoplastics used in the resin constituent layer of this invention used the good ingredient. That is, when it was a polyethylene or ethylene-alpha olefin copolymer and was polypropylene resin about polyethylene system resin, the polypropylene resin or the ethylene-alpha olefine copolymer of low crystallinity was used. The retention test was performed for the obtained multilayer film under the 40 degree-C-90%RH environment, and the color tone change to the amount of moisture absorption was measured with the Olympus, Inc. colorimeter.

[0046]



About the check of the moisture absorption function of a resin constituent, the container which it fabricated [ container ] with injection molding (the outermost layer: gay polypropylene resin, resin constituent of innermost layer: this invention) separately, and made the screw screw type hollow container and inner container which are shown in drawing 1 unify at a back process was used. A container configuration is the cylindrical container of 2 (75000mm<sup>3</sup>) height of 60mm, and the area of base of about 1250mm, and the superintendent officer of a resin constituent layer is about 8g. Moreover, 10g of superintendent officers and thickness fabricated the container of an outer layer to about 1.5mm using the gay polypropylene resin knot. This container was loaded with the humidity sensor as shown in drawing 2, and the sir made from T&D also measured the humidity in a container accompanying container opening by the recorder.

[0047]

Moreover, this moisture absorption container is that a cap and an inner container repeat a closing motion activity, and it is checked that an inner container deforms so that it may understand, even if it sees drawing 1. Although this was for maintaining the sealing performance in a container, it evaluated considering the destructive behavior of the inner container accompanying the opening activity as physical properties on the strength (the number of closing motion 50 times).

[0048]

[A check of an indicator function]

<Example 1>

Using the resin constituent obtained using A-1 and B-1, the co-extrusion multilayer film was produced because a melt index uses the ethylene-alpha olefine copolymer of 4.0 as a support resin layer. A result is shown in drawing 3 and drawing 4.

[0049]

<Example 2>

The co-extrusion multilayer film was produced by the approach of example 1 publication so that B-1 might become 34 weight sections (about 20 wt(s)% as % of the weight) to the 100 in all weight section of A-1 and the above-mentioned ethylene-alpha olefine copolymer using the resin constituent obtained using A-1 and B-1 by diluting with the ethylene-alpha olefin copolymer using this resin as support resin further. A result is shown in drawing 3 and drawing 4.

[0050]

<The example 1 of a comparison>

It is the same as an example 1 except having used A-4 and B-1.

[0051]

<The example 2 of a comparison>

Except that the melt index used the block polypropylene of 6.0 as support resin using A-2 and B-1, it is the same as an example 1.

[0052]

<The example 3 of a comparison>

It is the same as an example 1 except having used A-1 and B-2.

[0053]

<The example 4 of a comparison>

It is the same as an example 1 except having made the rate of B-1 in a constituent into the 0.5 weight section.

[0054]

Although having a moisture absorption function is checked since examples 1 and 2 and the examples 1-3 of a comparison have blended the inorganic compound which has hygroscopicity also from drawing 3, from color difference change of drawing 4, it is an example 1 at the last saturation attainment time of a moisture absorption function, it is over  $\Delta E > 10$ , and a compounding ratio has  $\Delta E > 6$  also in the half example 2 about. These colors are clear and clear yellow, and can be changed with moisture absorption from a white condition to homogeneity by the whole constituent at clear yellow.

[0055]



Moreover, in the example 3 which blended usual low density polyethylene, it is  $\Delta E < 1$ , and slightly, although discoloration is carried out, it is applied to precision. Moreover, although it is set to  $\Delta E > 10$  when polypropylene resin is blended, discoloration is dark brown, and although it has an indicator function, it is accompanied by the exterior problem.

[0056]

As shown in the example 3 of a comparison, when the silica gel which blended the cobalt chloride was used, it is  $\Delta E > 15$  and became purplish red from blue vividly according to moisture absorption, but since only the blended inorganic compound has discolored, if there was concentration nonuniformity by the distributed nonuniformity of an inorganic compound and it saw microscopically, since the inorganic compound itself would have discolored, the discoloration section looked granular and was accompanied by the poor appearance.

[0057]

[A moisture absorption function and evaluation of physical properties on the strength]

<Example 3>

The resin constituent used in the example 1 was fabricated as an inner container. By considering the situation of breakage of the humidity in a container and the inner container in which it is shown whether the fall of humidity is possible as container breakage, 1 at that time, 10, and which when repeating \*\*\*\*\* business 30 or 50 times combine the following examples 5-7 of a comparison, and summarizes them in Table 1.

[0058]

<The example 5 of a comparison>

It is the same as an example 3 except having used the constituent obtained using A-3.

[0059]

<The example 6 of a comparison>

It is the same as an example 3 except having fabricated the resin constituent used in the example 2 of a comparison as an inner container.

[0060]

<The example 7 of a comparison>

It is the same as an example 3 except having fabricated the resin constituent used in the example 4 of a comparison as an inner container.

[0061]

[Table 1]

|      | 開閉数   |      |        |        |       |        |       |      |
|------|-------|------|--------|--------|-------|--------|-------|------|
|      | 1回    |      | 10回    |        | 30回   |        | 50回   |      |
|      | 容器内湿度 | 容器破損 | 容器内湿度  | 容器破損   | 容器内湿度 | 容器破損   | 容器内湿度 | 容器破損 |
| 実施例3 | 8%RH  | 無し   | 8%RH無し | 無し     | 8%RH  | 無し     | 9%RH  | 無し   |
| 比較例5 | 10%RH | 無し   | 9%RH   | クラック発生 | ⇒中止   |        |       |      |
| 比較例6 | 8%RH  | 無し   | 10%RH  | 無し     | 9%RH  | クラック発生 | ⇒中止   |      |
| 比較例7 | 70%RH | 無し   | 82%RH  | 無し     | 85%RH | 無し     | 85%RH | 無し   |

[0062]

Since it has a moisture absorption function as a resin constituent as shown in an example 3 and the examples 5-7 of a comparison, it is possible to maintain the humidity in a container with low humidity. Moreover, in the example 3, since it becomes clear yellow as mentioned above, having an indicator function is also checked. On the other hand, the effectiveness of a single site system ethylene-alpha olefine copolymer is acquired also in respect of physical properties on the strength, and having controlled generating of the crack of an inner container is checked by using the ingredient of a polyolefine plastomer field especially. Moreover, if there are few loadings of the inorganic compound which has a moisture absorption function like the example 7 of a comparison with a natural thing, a moisture absorption function is unmaintainable.

[0063]

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[Translation done.]

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] They are the mimetic diagram of the container used in the example, and a device accompanying closing motion.

[Drawing 2] It is the mimetic diagram of the configuration (sensor installation) of the container at the time of moisture absorption functional evaluation.

[Drawing 3] It is the graph which shows the moisture absorption behavior of an example and the example of a comparison.

[Drawing 4] It is the graph which shows color difference change of an example and the example of a comparison.

[Description of Notations]

a: Hollow container outside

b: Hollow container inside (inner container resin constituent layer)

c: Inorganic compound

d: Resin A

e: Cap

f: An inner container / cap seal part

g: Humidity sensor

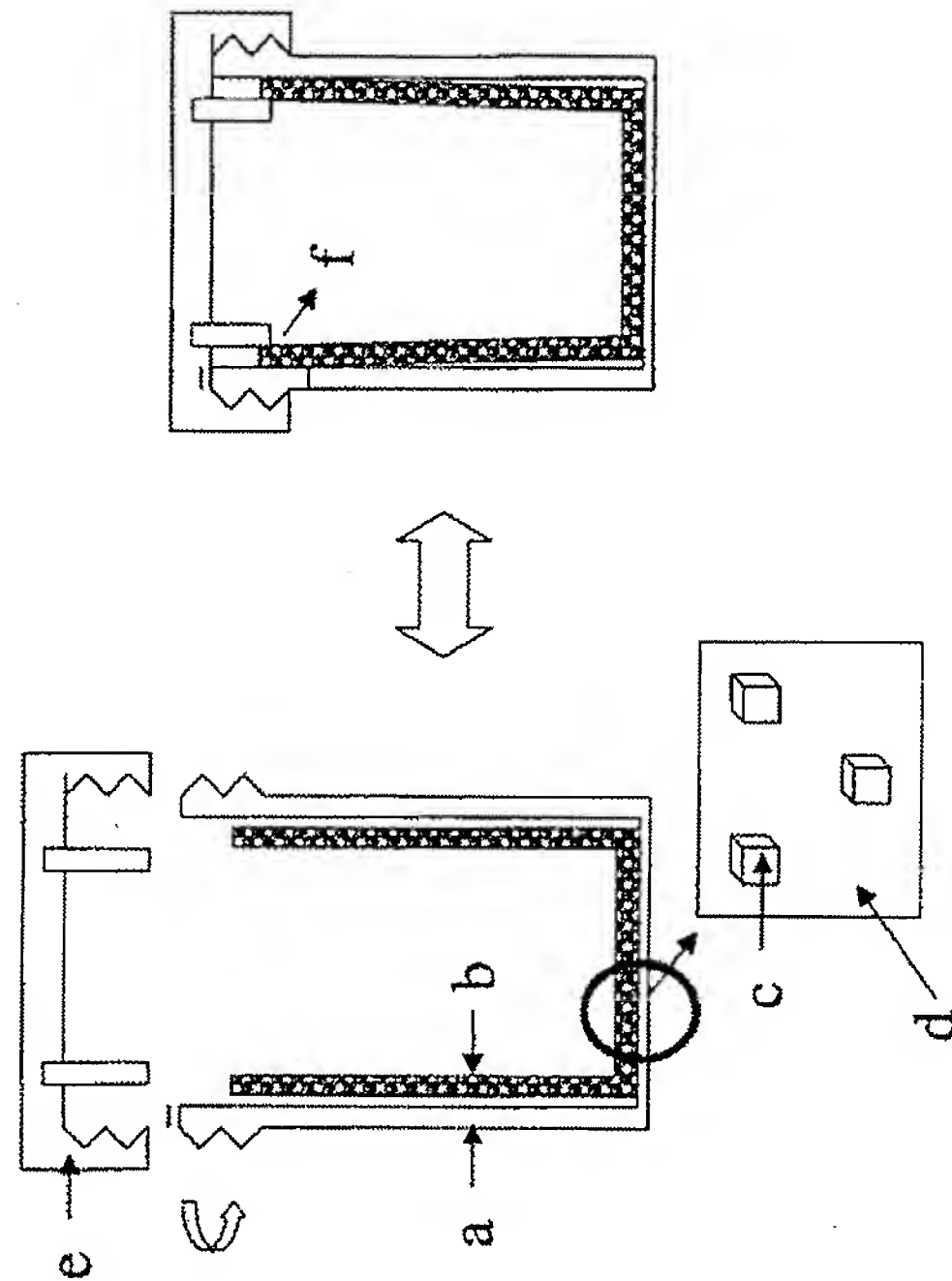
h: The binder section which fixes a humidity sensor and a cap

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[Translation done.]

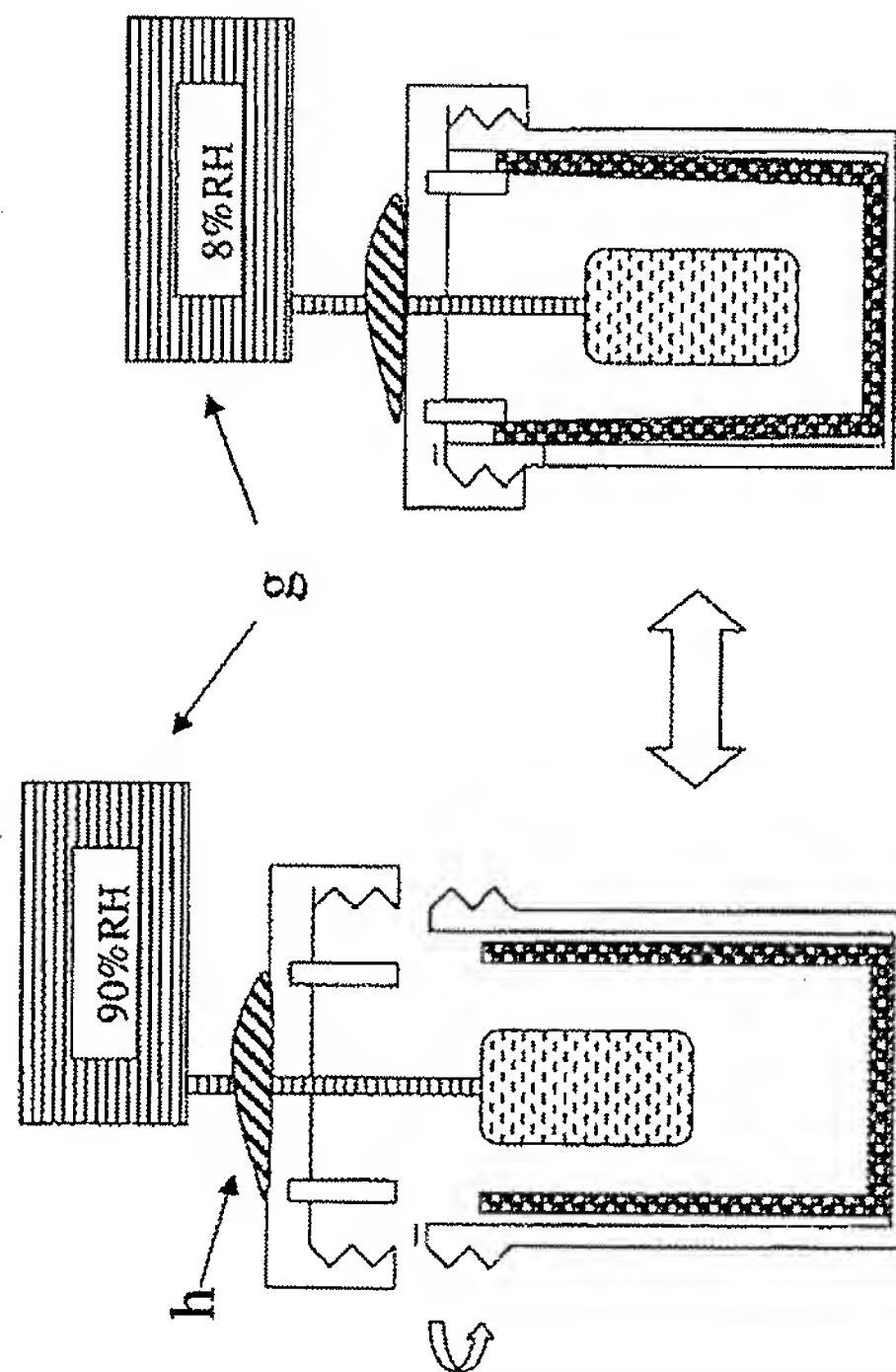


Drawing selection drawing 1



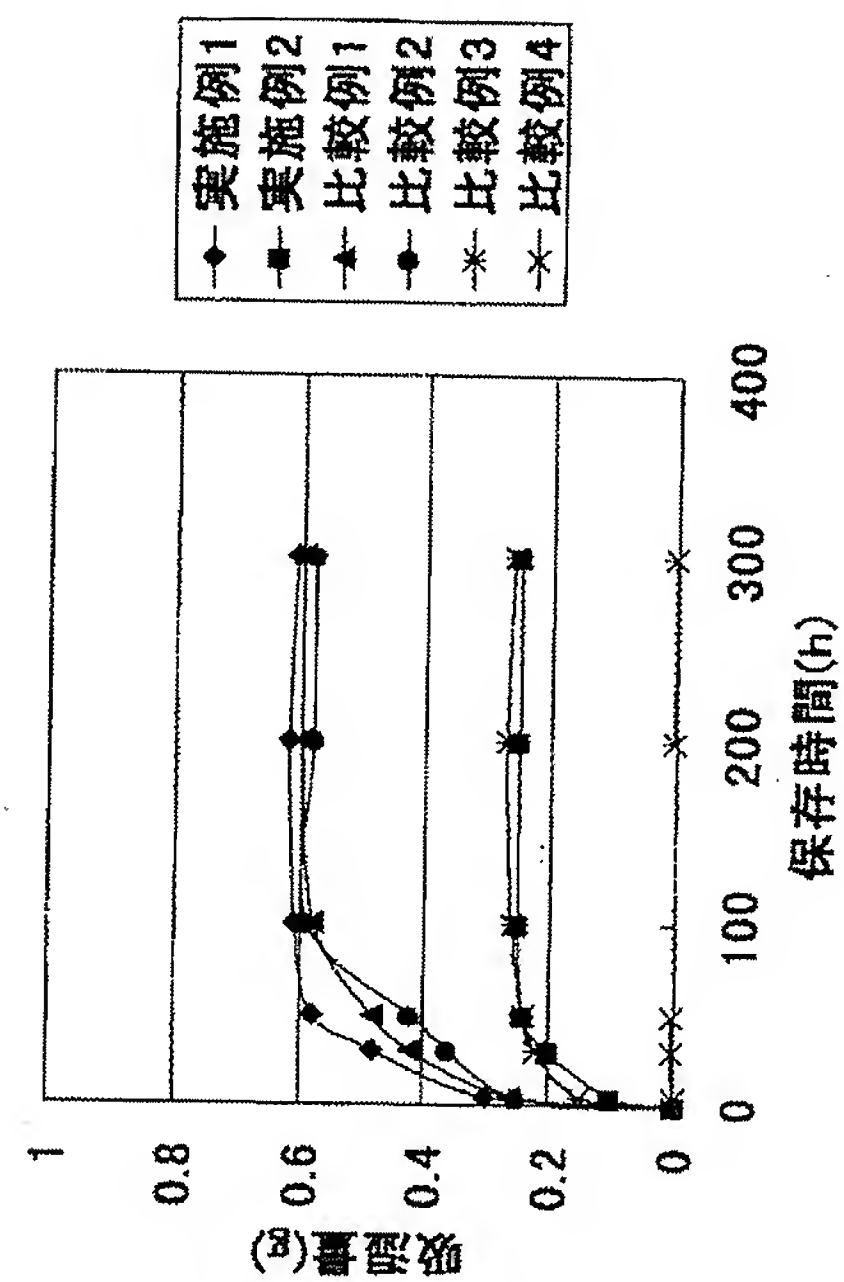
[Translation done.]

## Drawing selection drawing 2



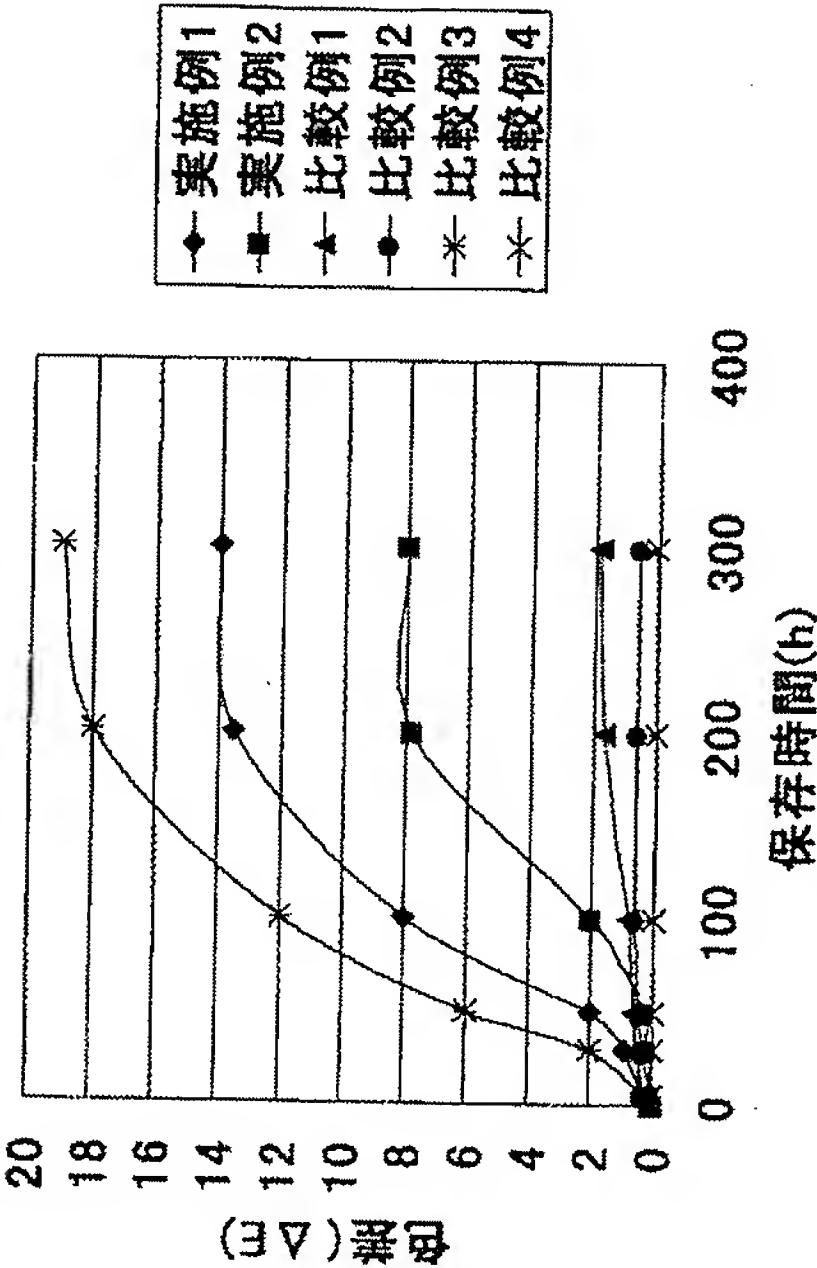
[Translation done.]

Drawing selection drawing 3



[Translation done.]

Drawing selection drawing 4



[Translation done.]